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# HIGH TEMPERATURE GAS THERMOMETRY

BY

ARTHUR L. DAY AND ROBERT B. SOSMAN

WITH

AN INVESTIGATION OF THE METALS

BY E. T. ALLEN

WASHINGTON, D. C.

PUBLISHED BY THE CARNEGIE INSTITUTION OF WASHINGTON

1911

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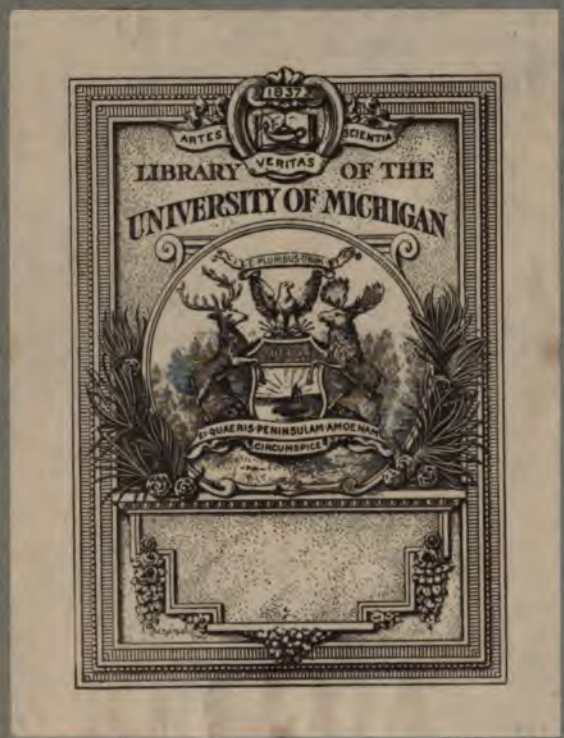


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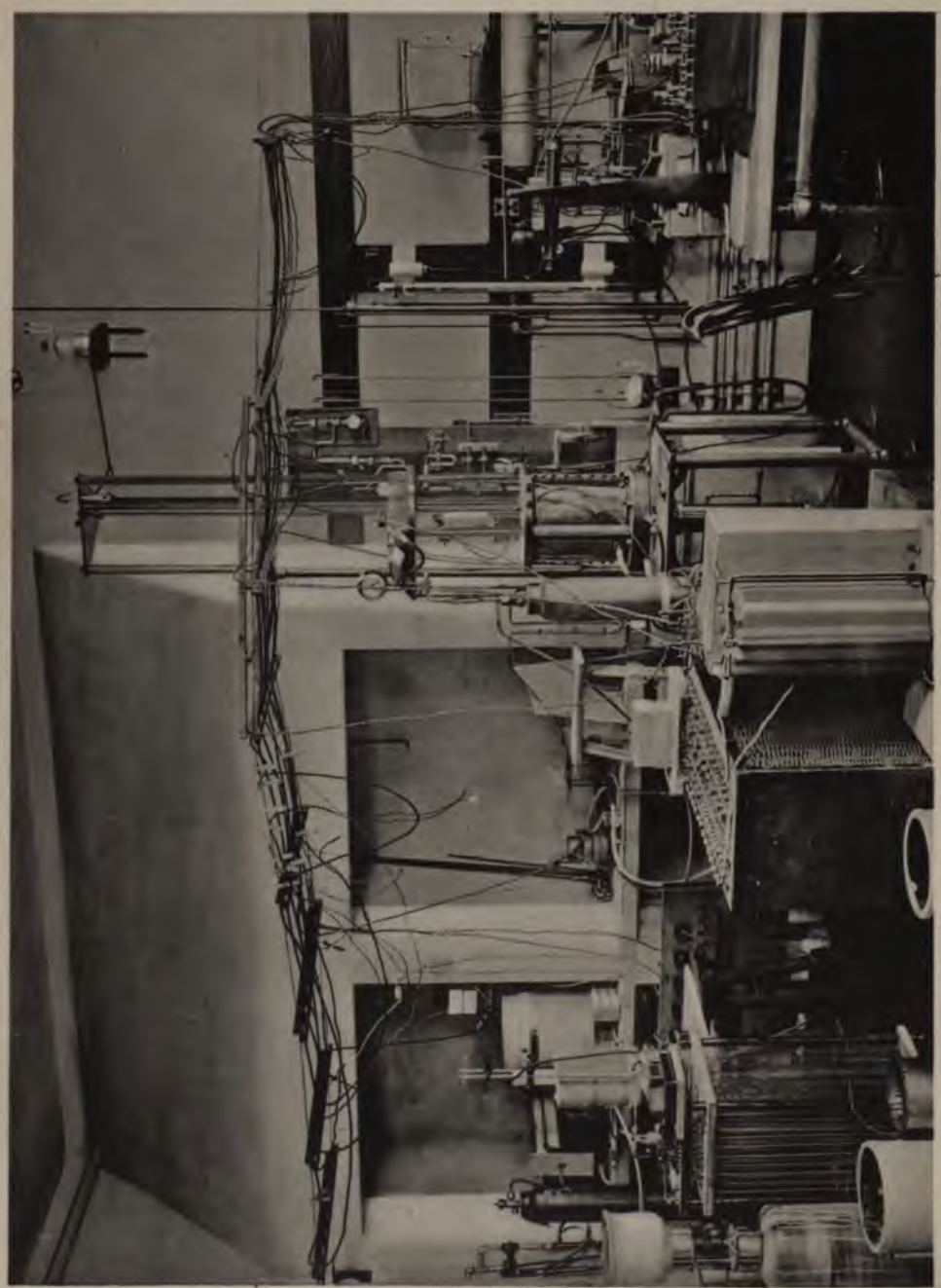


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# INTRODUCTION.

The year 1900 marked the close of an investigation of the gas thermometer at high temperatures which had been prosecuted with great vigor at the Reichsanstalt for nearly ten years. The temperature scale had not been extended beyond 1150° C., the stopping-place of most of the earlier investigations, but a scale had been established in which there was a strong feeling of confidence, and which is to-day in general use. The absolute accuracy was believed to be about 1° at 400° and 2° to 3° at 1150°. Temperatures higher than this were extrapolated by thermo-electric or radiation methods, at first with confidence, afterward with some misgiving, concerning which a good deal is said in the pages which follow. This scale and extrapolation scheme have never been formally adopted by international agreement, although no doubt such an agreement would have been of considerable value. In the absence of prescribed procedure the details of the extrapolation have differed considerably in the hands of different experimenters, which has caused an uncertainty in the interpretation of the higher temperatures, amounting to 50° at the platinum point. It was primarily for the purpose of clearing up this uncertainty in the region above 1150° and providing a sound basis of temperatures for the mineral work of this laboratory that this problem was taken up again.

The present investigation was begun in 1904 under the auspices of the U. S. Geological Survey and on the fourth floor of its building in the busiest portion of Washington. Here the conditions of light, constant temperature, and stability were very ill-adapted for quantitative work of the high order of accuracy to which it was desired to attain. It was therefore most fortunate for the success of this and other quantitative work which had hitherto been carried on with considerable difficulty, when the Carnegie Institution of Washington provided a new and well-equipped laboratory for it in 1907. The preliminary experimental work and all the measurements of the first series here described (to 1150°) were made in the Geological Survey; those of the second series, including all the observations of temperatures above 1150°, were made in the Geophysical Laboratory. The facilities provided in the new laboratory permitted measurements of great refinement.

Dr. J. K. Clement, who shared the burden of observations under the unfavorable conditions of the Survey building, withdrew in the spring of 1907 to become physicist of the Technologic Branch of the Survey (now the Bureau of Mines). The determination of the expansion coefficient of the platin-iridium bulb (p. 27), and all the work with the platin-rhodium bulb (p. 48 et seq.) was done by Day and Sosman.

If it is permitted to a student who has been actively at work upon this problem of high temperature measurement, partly in the Reichsanstalt and partly independently, for a nearly continuous period of fourteen years, to indulge in speculation of a somewhat irresponsible kind, this may be said apropos of the present status of absolute measurements of high temperature: The gas thermometer with a bulb of platin-rhodium is thoroughly trust-



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worthy and free from the large and more or less indeterminate errors characteristic of much of the earlier work, but the upper limit of temperature attainable with this bulb is nearly, if not quite, reached at 1550°. The platin-rhodium alloy is not rigid enough to be depended upon for constant-volume measurements at higher temperatures. The iridium bulb in use at the Reichsanstalt has the required stiffness, but can not be used for the calibration of thermo-elements at temperatures above 1550° without contaminating them beyond the possibility of restoration for accurate work. It may prove practicable to coat the surface of the bulb or the exposed wire with a viscous silicate or oxide which will prevent the sublimation of iridium, but all the efforts thus far made to find such a substance have been without success. And even if this proved successful it is unlikely that it would add more than 100 or 200 degrees to the existing scale.

A better plan might be to abandon platinum metals altogether in the near neighborhood of their melting temperature and to substitute tungsten or tantalum in a bath of stable oxides or silicates of sufficient fluidity to permit it to be stirred. Such a bath could perhaps be heated by passing the current directly through it, as in the barium chloride bath introduced by the General Electric Company a few years ago. Water-jacketing would protect the containing vessel, and a stirring mechanism and diminished pressure above the surface of the liquid, with a bulb of appropriate shape, would make it entirely practicable to maintain a nearly constant pressure inside and outside of the bulb. The bath would protect the bulb from oxidation and the stirring would provide a constant temperature about it—which is the greatest uncertainty in the present system of gas-thermometer measurement. All depends upon discovering a bath which will meet these difficult conditions. In a field which is still quite unexplored perhaps we need not altogether despair of finding it.

Meanwhile accurate gas thermometry up to 1550° insures the accurate calibration of optical and radiation pyrometers, which are well founded theoretically, convenient to use, and without an upper temperature limit. There is no need that the measuring instrument be in contact with the hot body whose temperature is desired, nor is it always necessary that any portion of the apparatus be heated to this temperature. The sensitiveness of most of these instruments is relatively low, but at extreme temperatures it is quite sufficient for industrial and probably for scientific uses also for many years to come. It would therefore appear that we are now well served in the matter of accurate and trustworthy high-temperature standards and convenient measuring devices, and if the need for a more extended and accurate scale shall arise it is by no means certain that the limit of standard temperature definition by means of the gas scale has been reached at 1550°.

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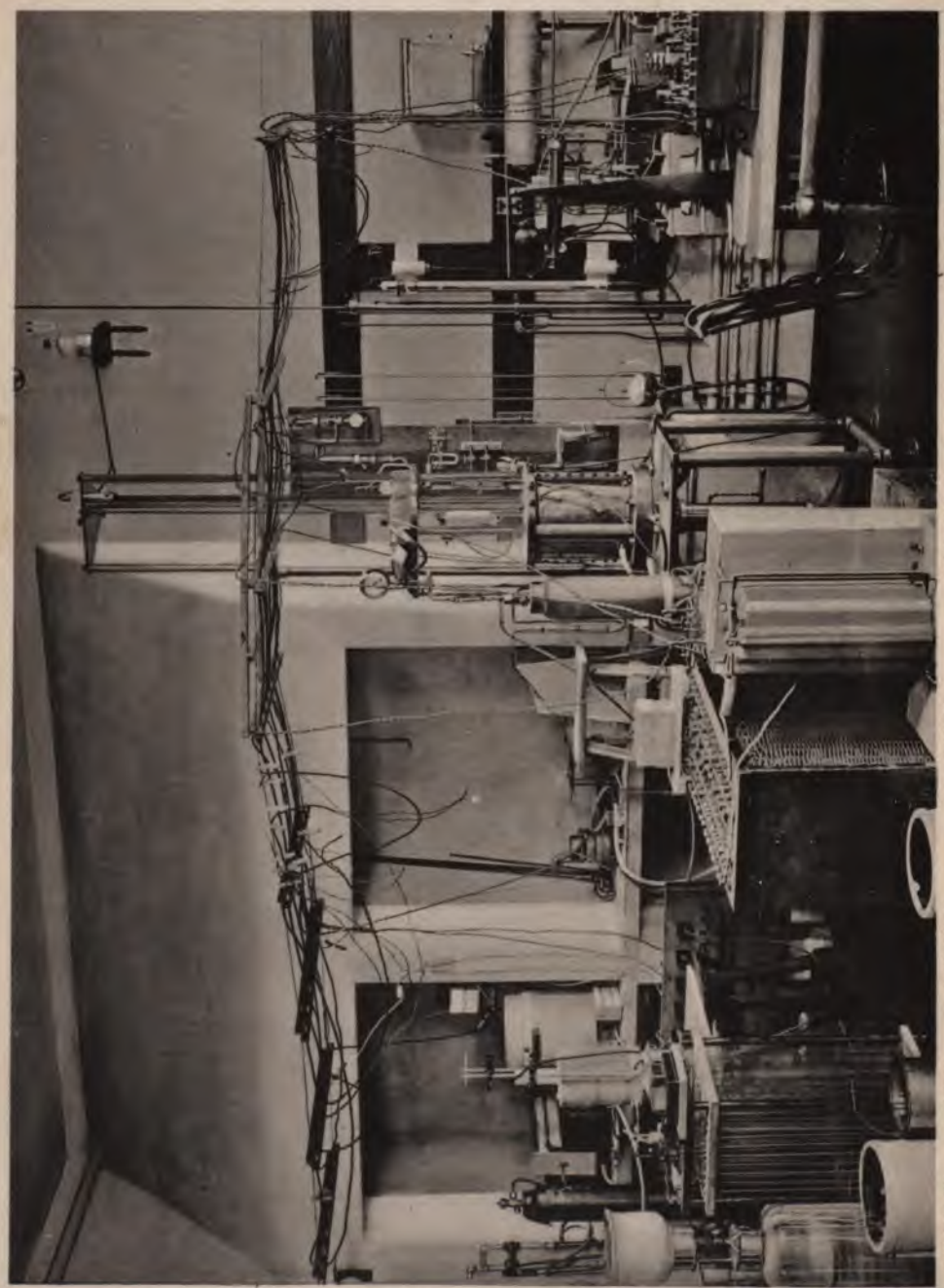


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# HIGH TEMPERATURE GAS THERMOMETRY.

## I. TEMPERATURE DEFINITION.

The measurement of temperature differs from most fundamental physical measurements in that the temperature function is not additive. There is no temperature unit corresponding to a foot-rule or meter-stick which can be applied successively to measure a high temperature as we would measure the height of a room. Two temperatures of one degree can not be combined in any way to give a temperature of two degrees. Temperature measurement is therefore wholly a matter of arbitrary definition, of selecting some convenient phenomenon (like the expansion of a gas) which varies continuously and as nearly as possible uniformly with temperature changes, of providing convenient arbitrary units of subdivision, and then of observing the expansion of the gas, or other phenomenon, under the conditions which surround the unknown body whose temperature is desired. The expansion of hydrogen has been established by international agreement as our fundamental measure of temperature. The gas thermometer is therefore now the standard thermometer in terms of which all temperatures are defined.

The theoretical interest in gas thermometry centers about the quantitative relation existing between the increase in the temperature of the gas expanding under constant pressure or volume and the quantity of heat required to produce it. It is a somewhat inaccessible question by reason of the difficulty of approaching it experimentally with the required accuracy. Although the amount of the expansion of gases is more closely proportional to the quantity of heat applied than that of liquids or solids, no strictly "perfect gas" in this sense has been found. The amount of the divergence between the expansion and the quantity of heat which produces it is slightly different with different gases, and is also slightly different for the same gas at different temperatures. In the case of nitrogen, which has a greater range of practical utility than other gases thus far studied, the expansion curve diverges slowly from the regular curve of a perfect gas as the temperature increases, but the amount of its departure does not attain the magnitude of one degree centigrade until the temperature reaches 1100° or more, and the magnitude of this correction factor, if it is to be regarded as a correction factor, is probably of the same order as the observation errors of an actual gas thermometer in the present stage of its development. For this reason, these theoretical considerations, which have been admirably treated by Buckingham in a paper, "On the establishment of the thermodynamic scale of temperature by means of the constant-pressure thermometer" (Bull. Bur. Standards 3, 237, 1907), do not seriously affect the definition of an accurate and practicable high-temperature scale by means of the gas laws.



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Buckingham defines the gas scales very clearly in this way:

"Two principal methods of gas thermometry are in use. In the constant-volume thermometer a mass of gas is kept at constant volume and its pressure observed at the melting-point of ice, at the condensing-point of steam (under standard atmospheric pressure), and at the temperature to be determined. If these three pressures be denoted by $p_0$, $p_{100}$, and $p$, the centigrade temperature according to the scale of this thermometer is by definition,

$$t_v = 100 \frac{p - p_0}{p_{100} - p_0}$$

The numerical value thus assigned to a given temperature depends slightly on the initial pressure and is somewhat different for different gases. * * *

"In the constant-pressure thermometer a mass of gas is kept at constant pressure, and its volume observed at the two standard temperatures and at the temperature to which a numerical value is to be assigned. If these volumes be $v_0$, $v_{100}$, and $v$, the centigrade temperature according to the scale of this thermometer is by definition

$$t_p = 100 \frac{v - v_0}{v_{100} - v_0}$$

The resulting value depends somewhat on the magnitude of the constant pressure and on the nature of the gas used."

Lord Kelvin has proposed, and the physicists who choose to consider the problem from the theoretical side (including Buckingham) have generally approved the proposal, to go further and interpret all temperatures strictly in terms of a hypothetical "perfect gas," in which the expansion (which defines the temperature), whether under constant volume or pressure, would increase exactly in proportion to the quantity of heat required to produce it. This would have the obvious advantage that temperature definition would become uniform and independent of the properties of any particular substance, but its adoption will be of little actual service to high-temperature thermometry until experimental measurements of greater scope and precision are available.

The direct experimental measurement of the degree of departure of an actual gas from this ideal state (the Joule-Thomson porous-plug experiment) involves the determination of two extremely small magnitudes which have not (as yet) been measured separately at all, nor together except with the greatest difficulty. From such results as we have it appears, as has been stated, that the difference between the expansion of the thermodynamically perfect gas and the actual expansion, from the low initial pressures usually used, of any of the gases hitherto employed for the purpose ($H_2$, $N_2$, CO, $CO_2$, $O_2$) approaches 1° at 1100°. Even for work of the highest precision, the constant-pressure or the constant-volume gas scale is therefore quite as serviceable as the thermodynamic scale, at the present stage of development of the subject.

By international agreement and nearly universal practice, two fixed temperatures are accepted as the basis of the modern temperature scale: The melting-point of pure ice and the boiling-point of pure water, both at normal atmospheric pressure (equal to 760 mm. of mercury). The interval included

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between these two temperatures is subdivided into 100 parts by measuring the constant volume expansion of hydrogen from an initial pressure of 1 m. of mercury throughout this interval.

The actual determination of these intervals or degrees centigrade was made by Chappuis at the Bureau Internationale des Poids et Mesures at Paris in 1888, and is a work of such painstaking character in most particulars that no investigator has found it necessary to repeat it since that time. The probable accuracy of the individual degrees thus determined, that is, of the international scale of temperatures between 0° and 100°, is stated by Chappuis to be 0.002.[1]

To extend the scale beyond these limits in either direction, it is (theoretically) only necessary to continue the measurement of the expansion of hydrogen under the same conditions down to or up to any desired temperature. In practice, this procedure encounters various experimental difficulties which increase rather rapidly as we go farther away from the temperatures of every-day life.

These experimental difficulties serve to place definite limits upon the accuracy of temperature measurement at present attainable in different parts of the field, of which it is important to obtain a clear idea in order to be able to form a sound judgment of the probable significance of measurements at widely different temperatures. If we are told, for example, that a solution boils at 90.27°, we recognize that this accuracy is entirely practicable. If, on the other hand, platinum is said to melt at 1755.46°, it is of advantage to know that the last two figures are wholly without significance, and the fourth is uncertain.

There is no denying the fact that a great deal still remains to be done upon the experimental side before the steadily advancing requirements of both science and industry in the matter of a trustworthy temperature scale, of sufficient accuracy and more particularly of sufficient range, can be satisfied. It is no disparagement of the present system of temperature definition to say that the gas thermometer itself is a complicated and cumbersome instrument to use in any of the forms which have hitherto been devised, and possesses limitations, both of range and accuracy, which are difficult to overcome.

One consequence of this, particularly in the region of high-temperature measurements, is that temperatures easily come to be regarded with unwarranted confidence in the hands of those who have never acquired a first-hand knowledge of these limiting conditions. This confidence has no doubt been fostered by the comparative ease with which *relative* measurements of temperature can be made, even in the more inaccessible parts of the scale, with the thermo-element and the resistance thermometer. These devices are sensitive to temperature differences of the order of magnitude of 0.01° throughout their entire range, but they are dependent absolutely upon fundamental measurements with the gas thermometer for their evaluation in terms of the generally accepted degree centigrade.

[1] In a recent paper, "Some new measurements with the gas thermometer" (Amer. Jour. Sci. (4), **26**, 405–463, 1908), the authors gave it as their opinion that the determination of the expansion coefficient of the thermometer bulb used by Chappuis, which is of course an important factor in the experimental problem, would not warrant an assumption of accuracy greater than 0.005°. To this Chappuis replied in a personal letter (1909) that considering all the factors of the problem, and subsequent experience, he still thought 0.002° a fair estimate of the probable error of the scale in the region between 0° and 100°.

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It is sufficiently obvious, though often carelessly overlooked, that no method of temperature measurement, however sensitive or adaptable it may be, can yield temperatures of greater absolute accuracy than the system in terms of which those temperatures are defined. With the gas thermometer as our basis of definition, therefore, we shall know our temperatures with just the certainty which it is able to furnish and no more. There is, to be sure, some justification for expressing the results of thermo-electric or resistance measurements in units smaller than the errors of the fundamental scale, where only comparative measurement is involved; but such measurements must not be used without regard to this limitation.

It is not the purpose of the present paper to discuss the general problem of thermometry, or the particular advantages of one system of thermometric measurement over another in laboratory or industrial practice, but merely to describe the work which has been done in recent years to increase the range and accuracy of the temperature scale, upon which the various devices for measuring high temperatures depend for their calibration. Neither is it necessary to include any discussion of the relative theoretical merit or experimental practicability of the constant-volume and constant-pressure methods of gas thermometry. The reader will find it in Buckingham's paper already mentioned, in Barus's review[1] of the progress of pyrometry for the Paris Congress in 1900, as well as in earlier discussions to which they have referred. The choice of the one or the other method is likely to be governed by the taste or predilection rather than by the necessities of the individual experimenter. Neither system possesses decided advantages over the other. Most of the recent measurements have been made with the constant-volume system.

## 2. HISTORICAL.

To reach a satisfactory estimate of the degree of confidence to be accorded to the new absolute measurements of high temperature requires some historical perspective, for the development of the experimental problem has now been going on for nearly a century. It will therefore be well to review somewhat briefly the chief steps in its progress for two explicit reasons: (1) In order that we may form a sound and properly critical judgment of the trustworthiness of the results so far attained; and (2) that future investigators may be enabled to avoid the limitations which have arisen in the earlier work.

We will therefore attempt to follow the development of the gas thermometer through some of the vicissitudes of its long service as a standard high-temperature measuring instrument. For it was understood from the beginning that the gas thermometer, with its cumbersome bulb and equipment, must always remain an instrument of reference rather than of practical utility.

*Prinsep, 1828.*—The first pyrometer based on the expansion of gases, so far as we now know, was made by Prinsep[2] and described by him in 1828. He used a bulb of gold, connected with a sensitive manometer with

[1] Carl Barus, "Les progrès de la pyrométrie," Rapports présentés au Congrès Internationale de Physique, 1900, vol. 1, pp. 148–177.
[2] Phil. Trans., 1828, 79-95; Ann. d. chim. et d. phys. (2), 41, p. 247, 1829.

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which to maintain the gas (air) at constant pressure within, and connected also with a reservoir of olive oil; the expansion of the air in the bulb displaced a proportionate amount of oil, which was caught and weighed and the temperature calculated. With this apparatus Prinsep made excellent temperature measurements, chiefly of the melting-points of the alloys of gold, silver, and platinum, which bear his name and are still sometimes used. The usefulness of Prinsep's thermometer was limited by the comparatively low melting temperature of the gold bulb.

*Pouillet, 1836.*—Prinsep was quickly followed by Sir Humphrey Davy and several others, all employing the expansion of air at constant pressure, but none contributing materially to the improvement of Prinsep's apparatus until Pouillet[1] constructed his instrument in 1836. Pouillet's bulb was of platinum, which enabled him to reach the highest temperatures, and his experimental procedure, with but slight modifications, is that employed to-day by Callendar and his associates, who have always expressed a preference for the constant-pressure method. It was Pouillet also who made and calibrated the first practicable thermo-element (platinum-iron), who anticipated the method of measuring temperature through determinations of the specific heat of platinum subsequently developed by Violle, and who made some study of the radiant energy sent out by glowing solids. In varying degree and with many of the inevitable limitations of the pioneer, Pouillet not only established gas thermometry upon a sound basis, but introduced several of the important practical methods of pyrometry (specific heat, thermo-electricity, radiation) which have been in use since his time.

Following Pouillet, therefore, the advancement of pyrometric measurement became to a considerable degree a question of perfection of experimental detail rather than of the development of new principles, and so, with one or two exceptions which will be noted presently, it has since remained. Regnault in particular made a number of improvements in the Pouillet instrument in 1847.[2]

The first gas thermometer which measured the expansion of the gas under constant volume appears to have been built by Silbermann and Jacquelin in 1853, but it was only indifferently successful. Effective use was first made of the method in the work of Becquerel described below.

*St. Claire-Deville and Troost,[3] 1857.*—It was soon after this that a real catastrophe occurred in the development of the gas thermometer. Deville and Troost (1857), desiring to use a heavier gas in place of air, introduced iodine into a bulb of porcelain and made determinations of a number of constant temperatures, most conspicuous among which, in the discussion which followed, was the boiling-point of zinc, which they ascertained to be 1040°.

*Edmond Becquerel,[4] 1863.*—Becquerel followed in 1863, using the Pouillet apparatus with platinum bulb and air as the expanding gas, and reached the conclusion that zinc boiled at 932°, more than 100° lower. In the controversy which followed, and which was maintained from both sides with considerable bitterness, these observations were repeated by both observers

[1] Compt. rend., **3**, 782–790, 1836.
[2] Relation des Expériences, Mem. Acad. Sci., Paris, **21**, p. 168, 1847.
[3] Deville and Troost; Compt. rend. **45**, 821–825, 1857; **49**, 239–242, 1859; Ann. d. chim. et d. phys. (3), **58**, 257–299, 1860.
[4] Ann. d. chim. et d. phys. (3), **68**, 49–143, 1863.

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with substantial confirmation of the first results, Deville and Troost maintaining from experiments of their own that Becquerel's platinum bulb was permeable to hot gases and that his results must of necessity be too low. To this contention Becquerel replied convincingly by using a porcelain bulb himself (still retaining air as the expanding gas), with both the constant-volume and constant-pressure methods of measurement, and announced a result (891°) even lower than his previous determination. Notwithstanding this, Deville and Troost were unwilling to regard the result as conclusive, and looked upon the discrepancy between Becquerel's earlier and later results (932° and 891°) with unconcealed suspicion. They reiterated their belief that the platinum bulb was permeable and that Becquerel's results with porcelain bulbs were still too low through failure to expose the bulb directly to the zinc vapor. Becquerel's bulb had been shielded from the direct action of the zinc by a protecting tube. Deville and Troost then repeated their own measurements and confirmed their earlier result. Becquerel, following, insisted that his measurements with the platinum bulb were not seriously affected by permeability to hot gases, a property with which he appeared to be familiar, and explicitly criticized the use of iodine by Deville and Troost.

The discussion ended here for the moment, without a decisive issue, but subsequent experience has substantially confirmed Becquerel in his contention and his numerical results. The high value obtained by Deville and Troost was undoubtedly due chiefly to the dissociation of the iodine at high temperatures, but this was not discovered until afterward in 1879 by Victor Meyer.[1]

The real catastrophe in the development of the gas thermometer, however, does not lie in the uncertainty of the results obtained with it by these distinguished observers, nor yet in the subsequent discovery that iodine is an inappropriate expanding medium with which to measure temperature; but rather in the discredit in which the platinum bulb came to be held and the universal substitution therefor of porcelain—a material of wholly uncertain chemical composition and physical characteristics. This was a backward step which was not retrieved for more than thirty years.

Deville and Troost[2] then entered upon a long series of experiments with porcelain glazed inside and outside with feldspar, in the course of which it appeared that the expansion of the bulb, a factor of great importance both then and now in gas thermometry, was variable with the temperatures to which it had previously been exposed. These irregularities diminished with continued use and were thought to become negligible in bulbs of Bayeux porcelain after a few heatings to a very high temperature.

*Regnault*,[3] *1861*.—During the period of this investigation Regnault was at work upon a displacement method (boiling mercury in an iron flask and estimating the temperature from the quantity remaining in the flask after cooling), which did not prove satisfactory. Schinz, Berthelot, and Weinhold suggested some modifications of this and other contemporary methods, but none of them proved of permanent value.

[1] V. and C. Meyer, Ber. Deutsch. Chem. Ges., **12**, 1426–1431, 1879. V. Meyer, ibid., **13**, 394–399, 1010–1011, 1880.
[2] Compt. rend. **57**, 897–902, 1863; **59**, 162–170, 1864.
[3] Ann d. chim. et d. phys. (3), **63**, 39–56, 1861.

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*Erhard and Schertel*,[1] *1879*.—Erhard and Schertel redetermined the melting temperatures of the Prinsep alloys in 1879, using a bulb of Meissen porcelain and air as expanding gas with considerable success. Their work contributed little of novelty, but was carefully done and the results have since been extensively used.

In 1880 Deville and Troost reappeared in the field, after a long silence, and also proposed a displacement scheme containing some improvements over the apparatus proposed by Regnault. Nitrogen was here used in place of air, but otherwise the method possessed insufficient accuracy to secure for it general approval. In the same year they published a summary of all their work on boiling zinc, giving 942° as the mean of 27 determinations, which was (for that time) in good agreement with Becquerel's first value, 932°.

*Violle*,[2] *1882*.—In the same year (1882) Violle, using Deville and Troost's methods and apparatus, found zinc to boil at 930° and thus added a further degree of probability to the determination of Becquerel. Violle continued his researches by determining with the gas thermometer the specific heat of platinum for a number of temperatures up to 1200°, and then extrapolating with this constant for the measurement of temperatures beyond the reach of the thermometer itself. He thus determined the melting-point of gold (1045°), of palladium (1500°), and of platinum (1775°), constants which continued in general use as standard temperatures for some years.

In the decade between 1882 and 1892 contributions to gas thermometry and the measurement of high temperatures are few and unimportant, but work was begun in those years on both sides of the Atlantic which, for the experimental skill and persistence with which the experimental difficulties and limitations were pursued and successively overcome, surpasses any effort which has been made either before or since that time. These were the investigations of Barus at the U. S. Geological Survey in Washington and of Holborn and his colleagues at the Reichsanstalt in Charlottenburg.

Barus[3] (1889) recognized, as no observer who preceded him had done, the superlative importance of a uniform temperature distribution about the gas thermometer bulb for purposes of high-temperature measurement, and he took the most extraordinary precautions to maintain it. A temperature of 1000° C. or more is not attained without very steep temperature gradients in the region immediately surrounding the zone of highest temperature. It is therefore a problem of great difficulty to introduce a bulb of from 10 to 20 cm. in its largest dimension into this hot zone without leaving some portion of it projecting out into a region 200° or 300° lower in temperature. Burning mixtures of gas and air for heating purposes also contributed to the irregularity and uncertainity of the temperature distribution about the bulb. Barus sought to avoid this by a method of great ingenuity, but also of great technical difficulty. He inclosed his bulb within a rapidly revolving muffle which by its motion protected every portion of the bulb from direct exposure to a particularly hot or a particularly cold portion of the adjacent furnace. This complicated furnace structure and consequently inaccessible

[1] Jahrb. f. Berg-u. Hüttenwesen (i. Sachsen), 1879, p. 154.
[2] Compt. rend., **94**, 720–722, 1882.
[3] Bull. 54, U. S. Geol. Survey, 1889. Die Physikalische Behandlung und die Messung hoher Temperaturen. Leipzig, 1892.

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position of the bulb made it impossible to introduce into the region about the bulb the substances whose temperature constants were to be measured and compelled him to use thermo-elements which were first calibrated by exposure in the furnace with the bulb and then used independently to measure other desired temperatures. The thermo-element has continued in general use in this intermediary rôle since that time.

*Barus and the Thermo-element.*—In the preparation and use of thermo-elements Barus also made much more extensive and elaborate studies than any one who has followed him. He first investigated a great number of substances, both pure metals and alloys, and measured and tabulated their electro-motive forces for different absolute temperatures. From these an element made from pure platinum and an alloy containing 90 parts platinum and 10 parts of iridium was finally selected for his standard work. The wires of this thermo-element were passed through the axis of the revolving muffle and into a re-entrant tube in the bulb of the gas thermometer, where the hot junction was brought to lie in the geometrical center of the spherical porcelain bulb. Here its electromotive force was read for a considerable number of measured temperatures and its curve determined. If the wires became contaminated by exposure to furnace gases they were melted and redrawn. This plan was pursued most conscientiously and a considerable number of temperature constants from the melting-point of zinc (424°) to the melting-point of gold (1093°) and of copper (1097°) determined.

It is an unfortunate accident that history has failed to record Barus's name along with that of Le Chatelier[1] in the development of the thermo-element for purposes of high-temperature measurement. It hardly admits of question that Barus contributed incomparably more to our knowledge of the thermo-electric properties of the different metals and their use than his distinguished French contemporary, but the 10 per cent iridium alloy which he finally selected proved to be less serviceable than the 10 per cent rhodium alloy developed by Le Chatelier, probably by reason of the greater volatility of the iridium and a consequent slow change in its readings. And so we find the Le Chatelier platin-rhodium thermo-element in use to-day the world over, while the magnificent pioneer work of Barus remains but little known.

*Holborn and Wien, 1892.*—In the same year in which Barus published his final memoir on the gas thermometer and the thermo-element (1892) Holborn and Wien published a paper, "Ueber die Messung hoher Temperaturen,"[2] covering nearly the same ground in the same general way, but with somewhat different results. Both used air as the expanding gas, both used thermo-elements to transfer the standard gas temperatures over to the substance to be measured; but Holborn and Wien attained to higher temperatures (above 1300°), while Barus took much greater precaution than his German contemporaries to secure a uniform temperature about his bulb. The arrangement adopted by Holborn and Wien possessed the further advantage that the thermo-element was entirely inclosed within the bulb itself and so was well protected against the contaminating influence of furnace gases besides giving a truer record of the actual temperature

[1] Bull. Soc. Chim. 47, 2, 1887. Journ. d. phys. 6, 23, 1887.
[2] Wied. Ann. 47, 107–134, 1892.

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of the expanding gas. Over against this it should be stated that the volume of the unheated portions of their bulb and manometer connections, which then constituted the chief source of error in all gas-thermometer measurements, was dangerously large.

Barus obtained 1093° as the melting-point of gold, Holborn and Wien 1072°, a difference of very troublesome magnitude. With these may be compared the earlier value (1045°) obtained by Violle in 1882, and of Callendar (1061°), who extrapolated the readings of the platinum resistance thermometer from the sulphur boiling-point (444.5), where his gas-thermometer measurements ended.

After 1892 Barus turned his attention to other things, but Holborn and Wien published a second article[1] in 1895 confirming and extending their earlier results. By employing a specially refractory porcelain bulb prepared by Dr. Hecht, of the Königliche Porzellan Manufaktur, they were able to continue the gas measurements nearly to the melting-point of nickel, which was determined by extrapolation to be 1484°. Both Barus, and Holborn and Wien, continued the thermo-electric measurements up to the melting-point of platinum, the extrapolation yielding 1780° (Holborn and Wien) and 1855° (Barus) respectively.

*Holborn and Day,[2] 1899.*—With the advancing demands of science for trustworthy high-temperature measurements, these differences in the absolute temperature of the melting-point of gold, which is an ideal substance for a temperature constant, soon came to be regarded as unsatisfactory and the whole problem was again taken up at the Reichsanstalt by Holborn and Day, with a view to clearing up these differences. At that time the gas thermometer was in serious danger of falling into disrepute as a physical instrument of precision, and it came to be a common habit in meetings of scientific men to excuse particularly poor temperature measurements by remarking that they were made with the gas thermometer. Holborn and Day began by using bulbs of Royal Berlin porcelain, but, after the investigation had proceeded for a year or more, abandoned them definitely and permanently to return to the old platinum bulb of Pouillet, with an appropriate gas (nitrogen) which could not penetrate the bulb wall. A further improvement of inestimable value in attaining constant and reproducible conditions was made when electric heating-coils were substituted for gas. With this change the contamination of the thermo-elements through the action of combustion gases, the danger of one or other of these gases penetrating the bulb wall itself regardless of the character or the pressure of the gas within, irregularities of temperature about the bulb, and inadequate control of the heat supply, were all eliminated or much reduced in magnitude at a single stroke. A preliminary account of these results was published in 1899 and a final account in 1900, in which several metal melting points were established as points of reference for the high-temperature scale, which soon found general acceptance and are still almost universally used.

*Barus's Summary,[3] 1900.*—At the time of the meeting of the international congress of physicists held in connection with the Paris Exposition in 1900 Barus was invited to prepare a review of the history of pyrometry up to that

[1] Wied. Ann. **56**, 360–396, 1895.
[2] Wied. Ann. **68**, 817–852, 1899. Am. Journ. Sci. (4), **8**, 165–193, 1899.
[3] Rapports présentés au Congrès International de Physique, 1900, vol. 1, 148–177.

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time, in which the following table appears. It offers an excellent review of the progress of pyrometry up to that time.

| Investigator. | Year. | Silver. | Gold. | Copper. | Nickel. | Palladium | Platinum. | Iridium. |
|---|---|---|---|---|---|---|---|---|
| | | ° | ° | ° | ° | ° | ° | ° |
| Prinsep | 1828 | 999 | | | | | | |
| Pouillet | 1836 | 1000 | 1200 | | | | | |
| Ed. Becquerel | 1863 | 960 | 1092 | | | | | |
| Violle | 1879 | 954 | 1045 | 1054 | | (1500) | (1775) | (1950) |
| Erhardt and Schertel | 1879 | 954 | 1075 | | | | | |
| Barus | 1892 | 985 | 1093 | 1097 | (1517) | (1643) | (1855) | |
| Holborn and Wien | 1892 | 971 | 1072 | 1082 | (1484) | (1587) | (1780) | |
| Callendar | 1892 | (961) | (1061) | | | | | |
| D. Berthelot | 1898 | 962 | 1064 | | | | | |
| Holborn and Day | 1900 | 961.5 | 1064 | 1084 | | | | |

Values in parentheses are extrapolated.

To this table Barus's own determinations, which were omitted from the original, and the measurements of Holborn and Day,[1] which were published in the same year just after Barus's paper appeared, have been added. None of the temperatures above the melting-point of copper was determined by direct comparison with the gas thermometer. Violle's higher temperatures were obtained by extrapolation by means of the specific heat of platinum determined for temperatures below 1200°, and Barus's and Holborn and Wien's by continuing the curve of electromotive forces of their thermo-elements over the same range.

Since the beginning of the present century but four attempts have been made to reach 1000° C. with the gas thermometer. These may be taken up in the order of their publication as follows: (1) J. A. Harker (1904), using a porcelain bulb and nitrogen; (2) Jaquerod and Perrot (1905), using a bulb of "quartz glass" and various gases; (3) Holborn and Valentiner (1906) using one bulb of platinum containing 20 per cent of iridium and one of pure iridium, both with nitrogen as the expanding gas; and finally (4) Day and Clement (1908) and Day and Sosman (1910), using bulbs of platinum containing 10 per cent of iridium and 20 per cent of rhodium respectively. The last investigation forms the body of the present paper.

*Harker.*[2]—The work of J. A. Harker at the National Physical Laboratory (England) does not differ in any important particular from the work of Holborn and Day which immediately preceded it at the Reichsanstalt. His instrument was an exact duplicate of the Reichsanstalt instrument by the same maker (except that the bulb was of porcelain instead of platin-iridium), and has since been altered only in certain minor particulars which need not be recounted here. His experimental operations were painstakingly performed and the results all in substantial agreement with those of Holborn and Day.

*Jaquerod and Perrot,*[3] *1905.*—Jaquerod and Perrot sought to establish a high-temperature scale from which two of the important sources of uncertainty in previous work should be eliminated: (1) the uncertainty

[1] Ann. d. phys. (4), **2**, 505–545, 1900. Am. Journ. Sci. (4), **10**, 171–206, 1900.
[2] Phil. Trans. (A), **203**, 343–384, 1904.
[3] Arch. d. sci. phys. et nat. d. Genève (4), **20**, pp. 28–58, 128–158, 454, 506–529, 1905.

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due to differences in the expansion of the various available gases; (2) any uncertainty which might enter the problem through the expansion of the containing vessel (bulb).

To accomplish the first object they prepared with the greatest care quantities of pure nitrogen, oxygen, air, carbon monoxide, and carbon dioxide, and used these successively for determinations of the melting-point of pure gold. To accomplish the second they selected for the material of their bulb a substance whose expansion coefficient was less than one-tenth as great as any which had been employed for the purpose up to that time. Both improvements afforded most valuable information. The five gases with appropriate corrections for their individual pressure coefficients gave the same temperature for gold within very narrow limits of experimental error and the bulb proved impermeable to all the gases and of very low and regular expansion for the temperature range employed. Its limitation lay in the fact that the silica bulb can not be used for temperatures above the melting-point of gold.

The relative accuracy of the individual measurements with this system ($\pm 0.2°$) was perhaps higher than has ever been attained with the gas thermometer,[1] but the absolute value of the gold melting-point which they obtained (1067°) is considerably higher than any of the other recent measurements. Whether this is due to some inaccuracy in determining the constants of the (relatively large) unheated connecting space leading to the manometer, or to lack of uniformity in the temperature distribution about the bulb, or to insufficient data about the actual expansion coefficient of the quartz-glass bulb, or perhaps to an unfortunate combination of all of these sources of error, it is impossible for any one except the experimenters themselves to determine. Certain it is that their work has contributed in two most important particulars to relieve the technique of gas thermometry from the uncertainty which has hitherto surrounded it and has thus been of the greatest value to all who have followed or may follow Jaquerod and Perrot.

*Holborn and Valentiner*,[2] *1906*.—The experiments of Holborn and Valentiner contemplated another definite and important step in advance. Theirs was the first serious effort to extend the gas scale itself from 1150° C., where all previous investigations had been halted, to 1600° C. The difficulties confronting such an undertaking are obvious and of an insistent kind. Of the limited number of substances available for use as bulbs none is without serious limitations at these extremely high temperatures. Porcelain becomes soft and its walls both absorb and generate gas in prohibitive quantities; silica glass devitrifies; pure platinum is very soft and is permeable to hydrogen; when stiffened with iridium or rhodium it is the best material available; but the iridium is destructive to the thermo-elements, and the bulb is likely to develop leaks and is permeable always to hydrogen if but a trace of the gas or of water-vapor is about. Furthermore, the difficulty of maintaining a constant temperature about a bulb of 200 cc. capacity increases at these temperatures and the difficulty of measuring with thermo-elements within the furnace is greatly increased by the conductivity of all insulating material. It is also a matter of no inconsiderable difficulty to generate and to regulate

[1] Excepting of course Chappuis, who measured no temperatures above 600°. His magnificent work is therefore hardly within the scope of the present article.

[2] Sitzungsber. Berl. Akad., 1906; 811–817. Ann. d. phys. (4), **22**, 1–48, 1907.

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accurately the quantity of heat required for a bulb of this size under conditions where all electrical insulation begins to break down, and to protect the mercury manometer from so hot a furnace without removing it to an impracticable distance.

All these reasons and others of inferior magnitude, but often of exasperating pertinacity, contribute to the glory of Professor Holborn's splendid attempt to extend gas thermometry far out into this region, which had hitherto remained inaccessible to all the resources of the laboratory except the somewhat uncertain extrapolation methods. The bulb with which the highest temperature (1680°) was obtained was of pure iridium made for the purpose by that indispensable friend of all recent high-temperature research, Dr. W. C. Heraeus, of Hanau, Germany. It was small, only about 50 cc. in capacity, but held tight through several determinations of temperature reaching nearly to 1700°. The temperatures along the bulb were much less constant than for lower temperatures (differences of 60° on a bulb less than 10 cm. long), and many of the other difficulties noted above no doubt contributed something to influence the result, but the effort demonstrated beyond peradventure that the extension of the gas scale to 1600° is practicable. The result gave melting palladium a temperature of 1575°.

This closes the account of the progress of gas thermometry down to the present undertaking, which was begun in 1904, and so overlaps only the work of Holborn and Valentiner, to which it bears a close relation, as will be explained presently.

## 3. IMPORTANCE OF ABSOLUTE MEASUREMENTS ABOVE 1150.°

This effort to reach an absolute determination of the temperatures lying between 1200° and 1600° has been chiefly inspired by two conditions. The highest temperatures (above 1600°) are conveniently accessible only to those methods of pyrometry which are derived from the Stefan and Wien-Planck relations, grouped together for convenience under the name "radiation pyrometers." These methods differ among themselves somewhat both in principle and in application, but in general they are all characterized by common qualities. They do not require that the measuring instrument be in contact with the hot body and they are all of very low sensitiveness at the lower temperatures. Furthermore, they are comparatively convenient to use and may be said to have no upper temperature limit. These practical qualities are obviously of inestimable importance to all future pyrometric work, whether in laboratory or industrial practice. Like all other pyrometers, however, they depend for their calibration upon the gas scale and require to have their readings evaluated in terms of it.

Now it happens that these radiation pyrometers do not become effective as temperature-measuring instruments below a bright red heat corresponding to a temperature of perhaps 900° and consequently they overlap the accurately measured portion of the gas scale for purposes of comparison and calibration only in the comparatively short interval lying between 900° and 1150°, above which the radiation scale is often extrapolated beyond 3000°, or more than seven times the interval of measured temperatures. This is obviously very uncertain procedure, the more so perhaps because the

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radiation pyrometer is at its lowest sensibility in this 250° region in which the calibration requires to be made. It would therefore add immensely to the stability and trustworthiness of the radiation methods if the gas scale could be extended 200° or 300° farther into the domain of radiation pyrometry with proportionate accuracy. To be sure, we have the thermoelement which overlaps both regions—the gas thermometer from very low temperatures to 1150° and the radiation methods from 900° to the melting-point of platinum (1755°)—but it also depends directly upon the gas scale, and extrapolation beyond this domain is fraught with equally grave uncertainty. Further consideration will be given to this difficulty on a later page (109).

The second reason for making a vigorous effort to extend the temperature-measuring standard to higher temperatures is more directly dictated by the requirements of the researches into the conditions of formation of minerals and rocks upon which this laboratory has now been at work for some years. It happens that the temperature region lying between 1100° C. and 1600° C. is the region in which the most important of the component minerals which go to make up the rocks are first formed, and in which therefore the temperature requires to be defined with great precision in order that the conditions of formation may be accurately known. In fact, a quantitative science of mineral and rock formation becomes possible only when such formation can be studied under known and accurately reproducible conditions, just as the problems of quantitative organic or inorganic chemistry are studied under known temperature conditions. Until very recently the minerals and the ore deposits have never been studied from this viewpoint, and our knowledge of their origin and relation to one another is inferential and very fragmentary when compared with contemporary knowledge of organic and inorganic chemical compounds.

This investigation was undertaken for these two reasons, then:

(1) To provide a broader range of absolute temperatures upon which to develop trustworthy pyrometric methods for general use in the great and increasingly important temperature region lying above 1000°.

(2) To attain much higher accuracy in the study of the conditions of mineral formation than has hitherto been possible.

It is perhaps noteworthy that this second reason for undertaking the present research is the same which inspired the investigation of Barus in 1892, which is in many respects the most comprehensive ever undertaken in this field. It offers additional reasons (if more were needed) why the existing generalizations of physics and physical chemistry should be extended over a wider range of temperatures and pressures. One of the most conspicuous grounds for the delay in attacking many of these obvious and generally recognized problems in geophysics lies in the fact that the measured relations established by the exact sciences have not been of adequate scope to meet the needs of large geologic or petrologic problems. The great body of physical and physico-chemical measurements have been confined to the region between 0° and 100°, while rock formation may have extended over a temperature region reaching to 1500° C. or higher. More embarrassing still is the fact that trustworthy data upon the effect of considerable variations of pressure upon most physical and physico-chemical relations

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are altogether lacking. It is therefore by no means certain that the generalizations hitherto regarded as established in quantitative physics and chemistry are directly applicable to problems of geophysical scope.

## 4. THE EXPERIMENTAL PROBLEM IN GAS THERMOMETRY.

The gas-thermometer problem is one in which theory is often inclined to lose patience with practice. It has been demonstrated over and over again, for example (Barus, loc. cit., Buckingham[1]), that the constant-pressure system of measurement ought to be more direct and free from error than the constant-volume system, notwithstanding which the major portion of the results which go to make up the real progress of the past fifty years has been obtained through the use of the constant-volume principle. Theory has also been very apprehensive from time to time of the ultimate outcome of attempting to define temperature in terms of the expansion of a diatomic gas, and yet nitrogen is the only gas which has yet been found practicable for long ranges extending to the higher temperatures. It does not react with a platinum bulb and does not diffuse through its walls, and so far (up to 1600°) no indication of the dissociation of nitrogen has been found. From the laboratory side of gas thermometry, the main difficulty is now, as it has always been, to find a practicable bulb which will hold some expanding gas without loss or change through a long range of temperatures and permit sufficiently accurate measurements of the pressure-volume relation within. After more than three-quarters of a century of the most varied experiences, pure nitrogen in a platin-iridium bulb in which the pressure at constant volume can be measured, was the only arrangement which had not yet encountered some very serious obstacle to the extension of its range or its accuracy. It was therefore adopted without hesitation for beginning the study here described.

If this somewhat circumstantially selected system does not at the moment appear to confront any insuperable obstacle, many and insidious difficulties have been encountered in the course of its development. One has only to examine the determinations of the same temperature made by different observers, all using substantially this method, to become convinced that some serious work still requires to be done to clear up the present uncertainty. The melting-point of gold is given by Barus (1892) at 1093°; by Holborn and Wien (1895) 1072°; Holborn and Day[2] (1901), 1063.5°; by Jaquerod and Perrot (1905), 1067.2°; by Day and Clement (preliminary, 1907[3]), 1059.1°. For the moment it is sufficient merely to call attention to these differences in the results which have been obtained, and to reserve detailed comment upon them for a subsequent part of the paper. Suffice it to say that both Holborn and Day, at the close of their work (1900) entertained the positive opinion that the discrepancies had occurred in the experimental details and were not chargeable to an oversight in any of the more fundamental relations involved.

With this prevailing idea in mind—that the general relations are already satisfactorily worked out and that the problem remaining is therefore pri-

[1] Bull. Bureau of Standards, 3, 237–293, 1907.
[2] Ann. d. phys. (4), 4, 99–103, 1901. Am. Journ. Sci. (4), 11, 145–148, 1901.
[3] Phys. Rev., 24, 531–532, 1907.

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marily an experimental investigation, (1) to increase the absolute accuracy of the measurements, and (2) to extend their range—Professor Holborn at the Reichsanstalt and Day and Clement at the Geophysical Laboratory took up the gas thermometer again in 1904. The details were for the most part independently planned and the work has been independently carried out. In a research which offers so many technical difficulties, two independent plants were obviously better than one. In so far as a division of labor was attempted, Professor Holborn entered at once upon the more daring undertaking, namely, to increase the range of measurement. He obtained a bulb of pure iridium in the hope that it might prove possible to make continuous gas-thermometer measurements as far as the melting-point of platinum. For this work the errors of observation were allowed to remain large, larger in fact than they had been in the joint work of Holborn and Day in 1900. The undertaking was entirely successful and yielded very satisfactory measurements up to about 1680°,[1] the error for the new portion of the gas scale (from 1150° on) increasing gradually to about 10° at 1600°.

The work at the Geophysical Laboratory was for the moment restricted to 1200° in an effort to eliminate or materially to diminish the errors which have been inherent in all gas-thermometer measurements up to this time. Progress is necessarily slow in work of this character, but we were chiefly delayed by having to build the entire equipment *ab initio*, except the bulb.[2]

The instrument which we constructed for this work has now been in operation for more than five years. It is of the constant-volume type, as has been explained, similar in general plan to that at the Reichsanstalt, but differing from it in certain important details with the especial purpose of correcting some of the known errors of the Reichsanstalt instrument:

(1) A uniform temperature along the thermometer bulb appeared to us imperative, and a much greater effort was made to obtain it.

(2) The entire furnace was inclosed in a gas-tight bomb in order that a nitrogen atmosphere might be maintained with equal pressures, both inside and outside of the bulb. This had the effect of obviating any tendency of the gas to diffuse into or out of the bulb, and allowed no opportunity for the deformation of the bulb through differences between the pressure within and without. A further effect of this arrangement was to increase the sensitiveness of the instrument fully threefold. It has been the practice heretofore in such temperature measurements to greatly reduce the initial pressure of the gas in order that its final pressure at the highest temperature to be measured may be substantially equal to the atmospheric pressure without, in order that the stress on the bulb through pressure difference may be least when its power to withstand such stress is smallest. In the Reichsanstalt instrument this restricts the available range of pressure for a temperature range from 0°–1150° to about 500 mm. of mercury, or less than 0.3 mm. per degree. By arranging to increase the pressure outside

[1] Loc. cit.

[2] The bulb which was used for the first series of measurements here recorded was one of two bulbs made by Dr. Heraeus, of Hanau, Germany, for the Holborn and Day investigation at the Reichsanstalt, one of which contained 20 per cent iridium and the other 10 per cent. The 20 per cent iridium bulb is still at the Reichsanstalt and was used in the investigations of Professor Holborn, to which reference has been made. The 10 per cent iridium bulb was exhibited by Dr. Heraeus at Paris in 1900, after which it was loaned to us for this investigation. The form and capacity of the two bulbs were substantially the same, about 200 cc. The authors take this opportunity to express their thanks to Dr. Heraeus for his most cordial and effective cooperation throughout this undertaking, and for his personal interest in the outcome of it.

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the bulb as the pressure within increases, this restriction falls away and it is possible to extend the pressure range over the whole length of the scale which the manometer carries. The scale of our instrument was 1.8 meters long. For a range of 1200°, therefore, we were able to work with a sensitiveness of a little more than 1 mm. for each degree centigrade, or rather more than three times the sensitiveness used in the Reichsanstalt instrument, and also to vary the initial pressure considerably without serious loss of sensitiveness. In order to reach 1600° this sensitiveness was subsequently reduced to about three-fourths of a millimeter per degree, which still gives opportunity for measurements of a high order of accuracy.

(3) In the capillary connecting link between the bulb and the manometer, we were able to diminish the volume of the unheated space to about one-third of its former value, and thereby still further to reduce one of the classical errors of gas thermometry. This "unheated space,"[1] it will be remembered, serves to connect the bulb which contains the expanding gas at a certain temperature and pressure with the manometer in which the pressure is measured. This space is therefore filled with gas which forms a part of the total gas content of the bulb, but is not heated with it and therefore requires a correction the magnitude of which has sometimes been so great as to create misgivings about the trustworthiness of the resulting pressure obtained.[2] The ratio of the volume of the unheated space to the total volume of the bulb $\left(\frac{v}{V}\right)$ in the final form of the gas thermometer used by Holborn and Day (1900) amounted to 0.0046; in the more recent instrument used by Holborn and Valentiner it amounted to 0.0042 with the 209 cc. platin-iridium bulb and 0.0181–0.0216 with the 54 cc. pure iridium bulb; in the Jaquerod and Perrot apparatus it reached 0.0178; while in our instrument it was reduced to 0.0015. The entire correction for the unheated space in our instrument therefore amounted to less than 4° at 1100° compared with about 20° in the older Reichsanstalt instrument and about 80° in the instrument used by Jaquerod and Perrot. An error of 10 per cent in the determination of the average temperature of the unheated space in our instrument will not therefore affect the result more than 0.4° at this temperature.

(4) The expansion of the bulb itself was redetermined with much greater care than heretofore.

All these are details of the utmost importance if a really accurate temperature scale based upon the expansion of a gas is to be established. The effect of a serious error in any one of the four particulars noted upon the temperature measurement is several times greater than that arising from differences in the expansion of the various available gases which formed the basis of the elaborate study by Jaquerod and Perrot, to which reference has just been made. And here, perhaps, lies the kernel of the whole matter so far as it concerns the establishment of accurate fundamental temperatures in a region as remote as 1000° from the fundamental fixed points. The interest of observers is easily diverted to questions of general and theoretical interest, like the validity of the Gay-Lussac law over great

[1] "Espace nuisible," "Schadlicher Raum."
[2] See in particular Jaquerod and Perrot, Arch. d. sci. phys. et nat., Genève (4), 20, pp. 28, 128, 454, 506, 1905.

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temperature ranges, while experimental conditions which permit errors of considerable magnitude in an absolute scale have had altogether inadequate attention. This is obviously no aspersion upon the beautiful work of Jaquerod and Perrot, or of any other investigator, but it may be the explanation of the prevailing uncertainty in high-temperature measurements. Jaquerod and Perrot, for example, in measuring the melting-point of gold with the gas thermometer, used five different gases successively in the same (fused silica) bulb, and came out with a maximum variation of only 0.4° for the entire series of observations, and yet in its absolute value the redetermination may easily be 5° in error. In fact, in one of their observations in which a porcelain bulb was substituted for silica, a difference of 4° was actually found. The observation was dropped, but it serves to direct attention sharply to a possible uncertainty of several degrees arising from the corrections for the distribution of temperature along the bulb and the unheated space, and for the expansion coefficient of the bulb itself.

## 5. APPARATUS.

Somewhat more in detail, the apparatus in use at the Geophysical Laboratory may be described as follows:

### FURNACE.

The furnace consists of a wrought-iron tube of about 25 cm. inside diameter, carrying a cast-iron pipe flange at each end. To these flanges cast-iron covers were fitted by grinding to a gas-tight joint. In position this bomb is vertical, and the lower cover is permanently secured in place with bolts. The furnace tube is made from a magnesite mixture,[1] is about 36 cm. long and 6 cm. inside diameter, and carries the furnace coil wound on its inside surface. This scheme of winding the heating coil on the inside of a refractory tube is very successful in its operation and is not difficult. With a pure platinum coil (melting-point 1755°) a furnace temperature of 1600° can be reached without danger to the coil and maintained for some time if desired. There is considerable loss of platinum through sublimation in maintaining a resistance furnace at this temperature, so that it is necessary to use a wire of considerable size if it is required to maintain so high a temperature for long periods of time. The gain over the same coil wound on the outside of a thin porcelain tube is about 200° (1600° instead of 1400°) for the same current and conditions of insulation.

The method of winding is simple. A series of five wooden wedges is grouped together so as to collapse when the center one is removed. When grouped and fastened together the outside surface is turned down to a cylinder of exactly the size which the finished coil is to have. This multiple wedge then serves as a collapsible arbor and the coil is wound upon it with any desired arrangement of turns. A piece of paper or thin cardboard between the wire and the arbor sometimes facilitates the removal of the arbor after completing the furnace. The arbor, with the coil upon it, is then placed in position in the cylinder and the remaining space between it and the cylinder wall is filled with magnesite cement of the same composi-

[1] Harbison-Walker Refractories Co., Pittsburg, Pennsylvania.

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tion (plus a little dextrine and water) as the tube itself. When this has set the arbor can be removed, leaving the coil in position in the tube. It then remains merely to go over the exposed wire with a very thin coating of the same cement and the coil is ready for use. Such a coil is less liable to displacement through expansion and contraction than when the winding is on the outside of the tube, for the expansion of the wire, instead of loosening the coils, merely causes them to sit the more tightly in place. We have had such coils in constant use for a variety of purposes in the laboratory for several years, and have found them durable, economical, and most convenient.

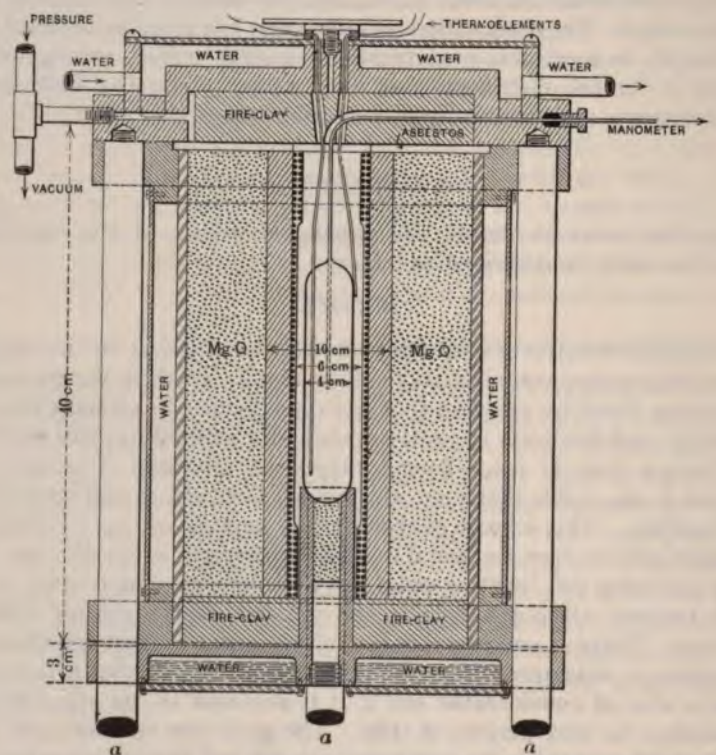


FIG. 1. A section through the gas-thermometer furnace (one-sixth natural size). The bulb is shown in position with the furnace closed ready for heating. The capillary tube connecting with the manometer passes out of the furnace through a packed joint at the upper right-hand corner. The thermo-elements pass through the center of the cover as indicated. The water-jacketing keeps the furnace sufficiently cool so that tight joints are readily obtained with ordinary rubber packing.

In this particular furnace the windings were somewhat closer at the top and bottom of the coil than at the middle, in order to provide a more uniform temperature from one end to the other. This scheme, although efficient, and perfectly satisfactory for most purposes, will not provide a perfectly uniform distribution of temperature over long temperature ranges. An arrangement of the turns which is adequate for low temperatures (500° to 1000°) will not provide sufficient compensation at the ends for much higher ones (1200° to 1600°). We therefore prepared two secondary coils of finer platinum wire in which the current could be independently varied, and

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mounted them within the main coil at the two ends of the tube. These coils extended into the tube about 7 cm. from each end and were fastened in position by smearing with magnesite cement as before. With this arrangement, we were able to obtain a temperature distribution along the bulb which did not vary more than 2° for any temperatures up to 1550°. To ascertain exactly what the temperature distribution was at the moment of any pressure measurement, it was necessary to use at least three thermo-elements simultaneously, one principal element at the middle of the bulb and secondary elements at each end. These elements were carried out of the furnace between two discs of rubber packing in the center of the cover.

The bulb was symmetrically located in the center of this furnace, the capillary stem extending out at the top of the heating tube and then with a gentle bend of 90° passing out of the metal bomb at the side of the cover, as can be seen in the diagram (Fig. 1). It was then connected by means of a second smaller capillary of platinum with the top of the manometer tube near the point of constant level adjustment. The iron bomb thus prepared was water-jacketed around the sides and at the top and bottom, which effectually prevented any of the furnace heat from reaching the manometer which stood immediately beside it. The scale and mercury columns of the manometer therefore suffered exposure to no temperature variation other than that which existed in the room, and any effect from the variation in the room was easily avoided by inclosing them in tubes of cardboard in which a rapid circulation of air was maintained with a water-jet pump.

When the furnace was mounted in position, the cover, from which hung the thermo-elements and the bulb, was permanently fixed upon three upright steel rods (*a a a*, Fig. 1). The body of the furnace bomb was then arranged to be lowered away from the cover by sliding upon two of the rods so as to expose the bulb and elements for ice- and boiling-point determinations before and after each heating. Fig. 2 shows the furnace body lowered in this way, leaving the bulb free and completely accessible for arranging an ice bath for the zero reading.

The apparatus is shown with the furnace open and ready for the ice-point determination. Hydraulic power served to raise and lower the furnace conveniently. When the furnace was raised for heating, a circle of bolts provided a positive pressure upon the top joint.

## MANOMETER.

The manometer was located about 35 cm. distant from the furnace and was of the usual U-tube type, constructed with a very heavy cast-iron base and light upper parts in order to render the mercury columns as free as possible from the vibrations of the building. The fixed point to which the mercury level was always adjusted occupied the usual position at the top of the short arm, the other arm extending upward for a distance of about 2 meters.

The scale, which was 1.8 meters long, was immediately beside the long tube, and was provided with a sliding vernier reading to 0.01 mm. It was of brass with a silver-plated band upon which the divisions were ruled, and had been calibrated by the German Normal-Aichungs-Kommission in

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Charlottenburg. The length of any portion of it was known in terms of the German standard meter to the nearest 0.01 mm. The scale was fixed in position below and arranged so as to expand upward through appropriate guides against a rubber cushion with the changes in the room temperature. The long manometer tube also passed through three guide screws at the top of the apparatus, which allowed it to expand and contract unhindered. Readings were obtained by means of two parallel knife edges on the vernier carriage, which could be brought to accurate tangency with the mercury meniscus by a slow-motion screw provided for the purpose. The mechanical construction was extraordinarily rigid and very satisfactory.

The temperature of the scale and mercury columns was obtained from three thermometers, each set in a short tube of mercury after the manner of Holborn and Day.[1] The upper tube with its thermometer could be moved up and down close beside the scale and mercury column, so as to give the temperature of the top of the longest column. The other two thermometers, each in its mercury cup, were fixed in position at the bottom of the long column and the top of the short column respectively. Both columns were surrounded with an inclosed air-tube about 5 cm. in diameter, in which the air was kept constantly and rapidly circulating about both mercury columns. The observed temperature differences along the mercury column sometimes amounted to 0.3°. This does not seriously affect the scale length, but the average temperature of the mercury column requires to be known to about 0.2°, with the high sensitiveness of this instrument, in order to bring the errors in the pressure determination within the desired limits—hence the three thermometers.

The mercury supply was contained in two basins, one a hollow steel bomb inclosed within the cast-iron base of the instrument, and the other a steel flask mounted upon the wall of the room near the ceiling and connected with the lower reservoir by a flexible iron tube. Cocks conveniently arranged admitted mercury whenever required. The fine adjustment of the mercury level was obtained by pressure upon a nickel diafram which formed the bottom of the lower steel reservoir. This diafram was about 12 cm. in diameter and could be raised slightly by the upward pressure upon its center produced by turning a milled hand-screw convenient to the hand of the operator. The lower reservoir was dome-shaped within and opened into a tube and stop-cock at its highest point, through which any air by chance imprisoned within the reservoir might be allowed to escape.

Gas was admitted to the bulb by means of the three-way cock (*A*, Fig. 4), leading to a supply of pure nitrogen, the pressure of which could be varied at convenience. It was also possible to exhaust the bulb through the same cock for the purpose of testing for leakage or rinsing the bulb.

## UNHEATED SPACE.

From the point of view of the errors of the instrument, the most important part of the manometer is the nickel cap at the top of the short arm which carries the fixed point for defining the constant volume. This cap is sealed into the glass manometer tube with ordinary sealing-wax of good quality, some care being taken that the sealing-wax fills all the cracks, which might

[1] Holborn and Day, "On the gas thermometer at high temperatures," Am. Journ. Sci. (4), 8, 170, 1899.

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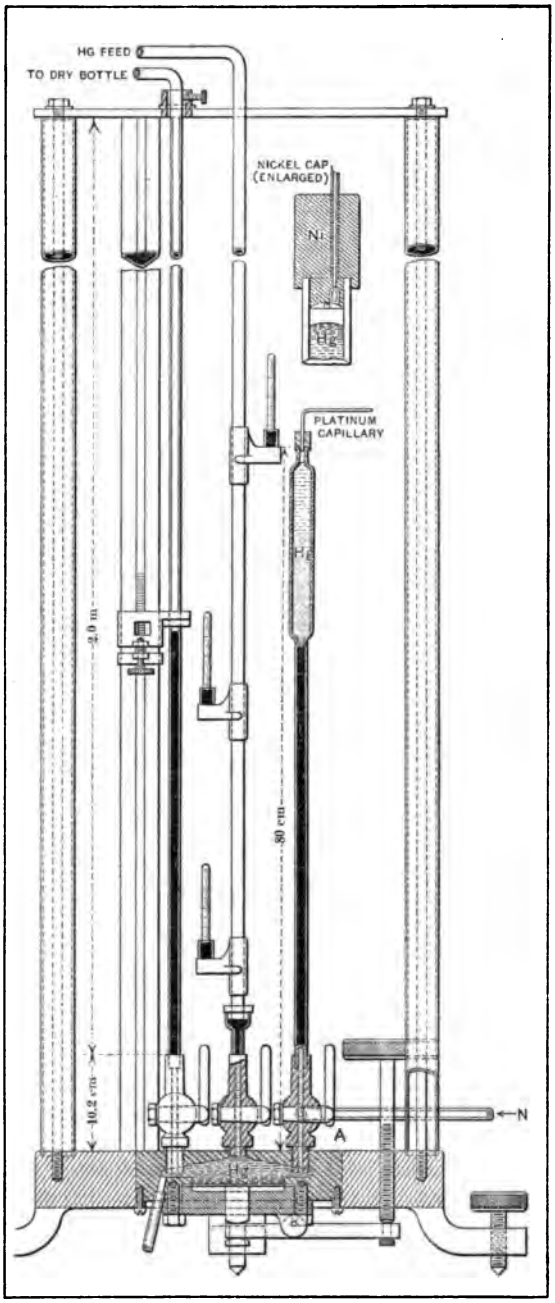


FIG. 4. A diagram of the manometer (about one-eighth size) showing construction and essential features only. Dimensions are approximate.

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otherwise retain gas and become a part of the unheated space. The under side of the cap is hollowed out slightly to conform to the shape of the rising mercury meniscus, and in the center a somewhat rounded point of nickel projects downward about 0.3 mm. When the column of mercury is raised in the arm until it becomes tangent to this point, the constant volume of the system is determined. This setting is made through a fixed magnifying microscope of some 20 diameters power. The portion of the "unheated space" included above the column is about 0.3 mm. thick, 1 cm. in diameter, and corresponds in form to the mercury meniscus.

The outlet leading to the bulb is a small opening beside the contact point containing a tiny valve of nickel about 1.5 mm. in diameter and 2 mm. long, with a ground joint at the top, which slides loosely in such a way that, if an accidental rise of the mercury column should tend to drive the mercury over into the bulb, this little nickel plug will be lifted by the mercury and automatically close the opening at the ground joint. This tiny valve opens into the capillary (0.55 mm. in diameter) leading outward to the bulb. Fig. 4 will show the construction more clearly. Where the space above the mercury column requires to be reduced absolutely to minimum volume some such protection is essential. If mercury once passes this opening, through accident or oversight, it reaches the bulb almost immediately, and once there it is a matter of two weeks boiling with nitric acid to get rid of it again.

Even with this valve, it sometimes happened that when gas was bubbled through the mercury in filling, even at the bottom of the tube some 80 cm. distant from the valve opening, tiny globules of mercury were shot upward with such speed and accuracy of aim as to pass up beside the little valve and into the capillary tube, after which their ultimate destination is inevitably the bulb. The altogether insignificant size of the opening and the distance required to be traversed by such a globule did not convey to us a suspicion that a globule might hit and pass it, but it actually happened on two different occasions, with the consequence of an exasperating delay.

In the present arrangement of the gas thermometer, this accident is also provided against by introducing a gold capillary instead of platinum, between the fixed point and the furnace bomb. Such microscopic globules of mercury are taken up by the gold without reaching the bulb and therefore remain harmless.

## BAROMETER.

It was deemed advisable from the start not to attempt to combine the barometer with the manometer, as has usually been done by the French observers and latterly in the Reichsanstalt instrument also. It is a convenient method and is rather necessary if a single observer is to make all the readings, but the combination brings three or four essentially different errors into one reading in a way that does not admit of a convenient evaluation of their individual magnitudes.

Two barometers were used throughout this investigation, both of Fuess manufacture and of the same type (Wild-Fuess normal barometer, 14 mm. tube). The corrected readings of the two instruments were in perfect accord and were correct in their absolute value within 0.05 mm.[1]

[1]One of these instruments was compared with the normal barometer at the U. S. Weather Bureau at Washington, the other was compared at the Bureau of Standards

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## THERMO-ELECTRIC APPARATUS.

The thermo-electric measurements were made with apparatus and by methods which have already been described in varying degrees of fulness in previous publications from this laboratory.[1]

Briefly, it may be noted in passing that all the thermo-electric measurements without exception were made with platinum-platinrhodium thermo-elements of Heraeus manufacture on a potentiometer of Wolff standard construction by direct comparison with a saturated cadmium cell. The cell first used was one of a series described in a previous paper,[2] which has been compared from time to time with the standard cells of the National Bureau of Standards and has never been found to contain an error greater than one or two parts in 100,000. In the later portions of the work other saturated cells courteously furnished by the Bureau of Standards for purposes of comparison were employed, and one Weston unsaturated cell. No errors or discrepancies from this source appeared during the entire investigation.

The galvanometer was a Siemens and Halske instrument of the usual moving-coil type. Later, a more sensitive moving coil galvanometer made by the Weston Electric Instrument Co. was advantageously substituted. With the help of a small rheostat in series with the galvanometer, its sensibility was maintained at a constant value such that one scale division in the telescope (distant 1.5 m. from the galvanometer) corresponded exactly to 1 microvolt in the thermo-element reading, which is roughly equivalent to 0.1°. In these galvanometers the wandering of the needle from its zero position was slight and never amounted to more than 0.2 or 0.3 of a scale division. Both were almost absolutely dead-beat with periods of five and three seconds respectively, so that adjustments for a temperature reading could be made with extraordinary rapidity and with an accuracy out of all proportion to the needs of the experiment.

The only error to which the thermo-electric observations were subject was the contamination arising from the iridium contained in the first bulb. During the first year in which these observations were begun the furnace coil also contained 10 per cent of iridium, but at that time the contaminating effect of this metal upon a thermo-element was not well understood. Later on, this coil was exchanged for a coil of pure platinum made especially for this purpose by Dr. Heraeus, which was guaranteed to contain no more than 0.05 per cent iridium and which was found upon analysis to contain considerably less than this quantity. Inasmuch as the furnace coil is always the hottest part of the system, this afforded considerable relief, but the position of the elements in contact with the bulb made it impossible to prevent some contamination above 900°, so long as the bulb remained bare. An attempt was made to reduce this difficulty still further by the use of a glaze made from melted mineral albite, which was appreciably soft at temperatures of 1100° but which appeared to prevent the sublimation of iridium so long as the coating remained continuous. The viscous material, however,

[1] Day and Allen, The isomorphism and thermal properties of the feldspars, publication of Carnegie Institution of Washington No. 31, 1905. Allen and White, On wollastonite and pseudo-wollastonite, polymorphic forms of calcium metasilicate, Amer. Journ Sci., (4), **21**, 89–108, 1906.
Walter P. White, Potentiometer installation, especially for high temperature and thermo-electric work, Phys. Rev., **25**, 334–352, 1907. Melting-point determination, Am. Journ Sci., (4), **28**, 453–73, 1909; Melting-point methods at high temperatures, Am. Journ. Sci., (4), **28**,, 474–489, 1909.

[2] Day and Allen, loc. cit., p. 26.

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showed a persistent tendency to gather together into globules, leaving bare spots on the bulb which were not wet by the glaze, so that this protection was not complete. Porcelain insulating tubes open at the ends afford little or no protection. We were accordingly driven to the conclusion that for the higher temperatures iridium must be banished from the furnace completely before consistent observations could be obtained. This is the chief reason why the first series was not extended beyond 1200°. The observations above this temperature will therefore be described on a later page (p. 48). For these later observations a bulb containing no iridium was substituted for the one described here.

Up to 1200° our precautions were sufficient to prevent serious contamination of the elements and the error due to such contamination as was unavoidable has been eliminated by frequent calibrations of the three elements used for each observation, either by comparison with standard elements known to be free from iridium contamination, or by melting-point determinations of standard metals. Toward the close of this first series, in order to establish absolute proof that the readings were not encumbered with systematic errors, however small, from this cause, an independent observation was made in the following way: The element at the middle of the bulb was replaced by a freshly calibrated new element known to be in perfect condition. After an ice-point determination and with all the precautions above described, the furnace was heated directly and as rapidly as possible to 1200°, where a single observation was made and the furnace immediately cooled down again. The new element was then removed from the furnace and recalibrated in order to establish beyond question the fact that it had suffered no contamination whatever during the short and rapid run. This independent determination, in which it was definitely proved that iridium contamination played no part, served to establish the absolute correctness of the high-temperature observations in so far as the error from this most persistent source was concerned.

No reason has yet arisen in any of the experiments with nitrogen for suspecting limitations of any kind due to the gas. It has shown no tendency to react with the platinum bulb or to pass through its wall or to dissociate at any temperature to which it has yet been carried in gas thermometry.

## THE BULB.

As has been stated with some emphasis in the historical introduction, the question of a suitable bulb to contain the expanding gas has been and is to-day one of the most serious which gas thermometry confronts. The first experiments (Prinsep) were made with a bulb of gold, which was soon abandoned because of its low melting-point. Following this, platinum was employed (Pouillet), but here a difficulty was encountered which eventually caused its abandonment in favor of porcelain on account of its supposed permeability to gases (Deville and Troost; Becquerel). But the porcelain bulb without glaze is itself porous; with a glaze it is a chemically undefined mineral mixture which not only softens below 1200° with more or less change of volume, but also gives out gas (either original or previously absorbed), so that the porcelain gas thermometer, as it is commonly called, never returns to its original zero after heating to high temperatures.[1] The uncer-

[1] Holborn and Day, Am. Journ. Sci. (4), 8, p. 185, 1899. Wied. Ann. 68, p. 843, 1899.

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tainty in the zero which arises through the use of the porcelain bulb causes an error in a single observation of the order of 5° at 1000°, which is practically impossible of satisfactory correction.

The return to metal bulbs is due to Professor Holborn of the Reichsanstalt, who has successfully used a platinum bulb (containing 20 per cent of iridium) of 200 cc. capacity with nitrogen as the expanding gas up to 1600° without discovering any irregularity in its behavior. A similar bulb of platinum containing 10 per cent of iridium was successfully used in this laboratory for nearly three years without developing any limitation other than that due to the contaminating effect of the iridium on the thermo-elements. It is a matter of great difficulty and some uncertainty to make trustworthy measurements of temperatures above 1000° with platinum thermo-elements in the presence of iridium (see paragraph on thermo-electric measurements preceding), even when the iridium is present only in a low percentage (0.05%) alloy with platinum. To obviate this a bulb of platinum containing 20 per cent of rhodium and no iridium was substituted for the iridium alloy in our later observations (p. 48) with marked success. The porcelain bulb has therefore probably disappeared permanently from gas thermometry.

Parenthetically, it may be remarked that the platinum crucibles and other ware as made up for laboratory use in this country are usually stiffened with about 2 per cent of iridium, a quantity amply sufficient to contaminate thermo-elements if exposed in the furnace with it to temperatures above 900°.

## 6. PLAN OF PROCEDURE.

The procedure followed in the first series of observations was substantially as follows:

With the body of the furnace lowered so as to expose the bulb, a pail of suitable size was brought up about the latter and filled with distilled water and finely divided ice in such a way as to inclose the bulb and so much of the capillary as was included within the furnace when hot. Several readings of the ice-point were then made on the manometer, together with simultaneous readings of one or both barometers. To control the expansion coefficient of the gas, these readings were occasionally followed by a second reading at the temperature of boiling water in which the ice pail was replaced by a double-chambered boiling-point apparatus of standard type. In general, however, it may be said that the expansion coefficient of pure nitrogen has already been so carefully determined by Chappuis and others that this observation is superfluous, particularly as the sensitiveness obtainable in a bulb of a size suitable for long ranges of temperature is not sufficient to admit of a determination comparable with theirs.

After the ice-point had been determined, therefore, the general procedure was to arrange the thermo-elements in position at the top, middle, and bottom of the bulb (Fig. 1), to close up the furnace gas-tight, and to proceed with the heating. Before turning on the current, however, it was our habit during the earlier experiments to exhaust the bomb and replace the air with a nitrogen atmosphere, the nitrogen being supplied from a separate bomb under high pressure. The nitrogen for this purpose was made in large quantities in the laboratory by the method of Hutton and

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Petavel,[1] and pumped into bombs at a pressure of about 1,000 pounds per square inch. One of these bombs could be readily connected with the furnace through appropriate portable connections and a reducing valve whenever desired. Later, compressed air was found to serve the purpose equally well. A pressure gage connecting with the inside of the furnace bomb enabled the pressure within the bomb, that is, outside the bulb, to be read at any time. If the advance in pressure outside the bulb did not proceed as rapidly as that within, additional nitrogen could be admitted if required. In general, it can be said of the operation of this arrangement for the adjustment of pressure within and without the bulb, that if the furnace is perfectly tight the two pressures advance together and are never very far apart. Attention to this detail is therefore not burdensome unless the bomb is leaking, in which case the losses must be supplied by the addition of small quantities of nitrogen from time to time. An effort was made to keep the pressure outside the bulb within one-half pound of the inside pressure as read on the manometer.

After the current had brought the temperature to the point where it was proposed to make a reading, about three-quarters of a hour was required to adjust the three resistance coils so as to produce a permanently uniform temperature along the bulb, which limited the number of temperatures observed in one working day to six or seven. It was therefore our habit to make readings, at 50° or 100° intervals, so as to cover a considerable range of temperatures each day. On following days intermediate temperatures were selected in such a way that the whole field would eventually be canvassed in steps of 25°. In order to provide a sufficiently rigid control of the conditions within the bulb, however, each day's readings began with a new determination of the ice-point.

It is interesting to note in passing that the variation of the ice-point after heating, which was a conspicuous feature in all gas-thermometric work previous to 1900, has now substantially disappeared with the return to the platinum bulb.

When the temperature had become constant over the entire length of the bulb, one observer took his position at the telescope of the manometer and the other at the galvanometer, and simultaneous readings were made of the group of thermo-elements and of the pressure within the bulb. Between each two pressure readings a reading of the barometer was made by the observer at the gas thermometer, the barometer having been arranged in a conveniently accessible position for that purpose. All the readings were arranged in symmetrical groups in such a way that the time rate of change of temperature, if any, would fall out in the arithmetical mean of the pressures and temperatures at the beginning and end of the series. At the beginning and end of this set of observations, readings were made of the three thermometers which gave the temperature of the mercury columns of the manometer. The temperature of the unheated space requires no separate determination, as the average room temperature was sufficiently accurate to determine the correction for the unheated space.

Following such a series, the temperature was increased by the desired interval and the same operation gone through again. Constant attention

[1] Hutton and Petavel, "Preparation and compression of pure gases for experimental work," Journ. Soc. Chem. Ind., 23, 87–93, February, 1904.

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was of course required in the meanwhile to see that in increasing the temperature of the furnace, and therefore of the bulb, the pressures inside and outside the bulb did not get too far apart. The same was true of the cooling at the close of the series.

Before the bulb was connected up with the manometer for the final filling, readings were made of the position of the fixed point which defines the constant volume upon the scale. This was done by letting in mercury with both tubes open and reading the mercury level in the long tube when the meniscus in the short tube was raised so as to be just tangent to the fixed point.

*Volume of the Bulb.*—The volume of the bulb, including the stem, was determined by weighing with water at the beginning of these experiments and again at their conclusion with the following results:

| | |
|---|---|
| Volume of platin-iridium bulb and stem, September, 1905.... | 195.79 cc. |
| Volume of platin-iridium bulb and stem, February, 1908..... | 195.66 cc. |

Since $V_0$ enters into the computation of temperature only as a part of the correction factor for the unheated space, and as this total correction is never more than 5°, it is obvious that the absolute volume of the bulb is not, of itself, an important factor in the problem. On the other hand, the correction for the expansion of the bulb with the temperature amounts to 45° at 1100°, and is the most important correction factor which requires to be determined. An error of 1 per cent in the determination of this constant ($\beta$) produces an error of 0.5° at 1100°.

## 7. EXPANSION COEFFICENT OF THE PLATIN-IRIDIUM BULB.

The determination of the expansion coefficient of the bulb did not prove to be the perfunctory operation which had been anticipated, but developed into an independent research of somewhat exasperating character, covering several months.

### APPARATUS AND METHOD.

There are two methods which might be pursued to obtain this constant. It is theoretically possible to determine the actual volume expansion of the gas-thermometer bulb in position in the furnace, but an effort to carry it out experimentally a few years ago developed serious difficulties where the range of temperature is so great and the accuracy required so considerable. We therefore preferred to obtain a bar made from the same material as the bulb, and to determine its linear expansion under conditions which were under more perfect control.

In principle, the method of procedure is the one used at the Reichsanstalt. A bar of platin-iridium 5 mm. in diameter and slightly more than 25 cm. in length was prepared for the purpose and heated in a tube furnace in which the temperature could be maintained nearly uniform from one end of the bar to the other and conveniently regulated up to 1000° or more. The ends of the bar were filed flat for a distance of 6 mm. and upon these flat surfaces millimeter divisions were ruled with a dividing engine. The balance of the apparatus consisted of a pair of micrometer telescopes mounted so as to observe these divisions and also to maintain a constant

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distance between the fixed cross-hairs from beginning to end of the experiment. Heating the bar then served to move the ruled lines past the fixed cross-hairs of the telescopes and the amount of the displacement was measured for any desired temperature.

The aggregate expansion of a 25 cm. bar over the interval from 0° to 1000° is about 2.5 mm. The telescope micrometers as they were focussed for the measurements gave about 450 divisions (each about 2 mm.) of the drum for 1 mm. on the bar, and in the individual readings differences of 0.2 or 0.3 of a division were readily distinguishable. It was therefore easily possible to make very accurate measurements of the expansion of such a bar by direct observation without the use of a contact lever or any multiplying device whatsoever.

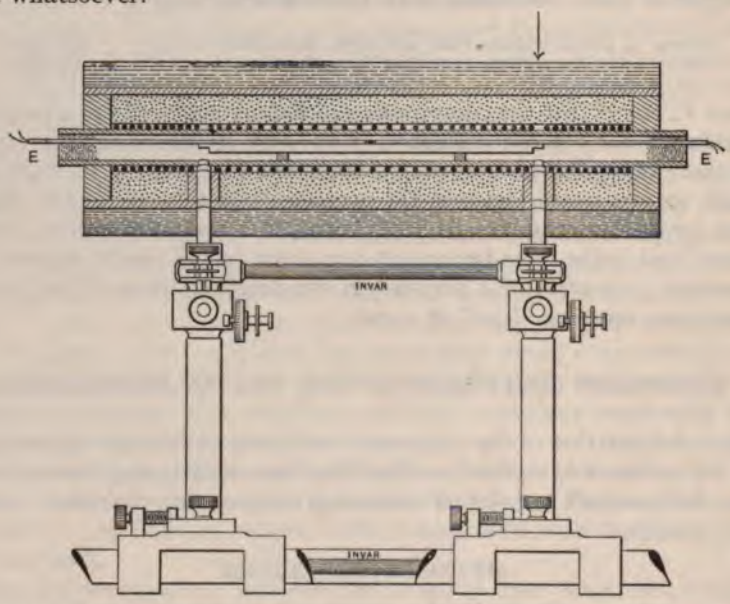


FIG. 5. Longitudinal section of the expansion-coefficient furnace, showing bar, thermo-elements (E, E), and microscopes in position. A section through the arrow is shown in Fig. 6.

The essential features of the apparatus can be partly seen from the figures (Figs. 5 and 6, and Fig. 3, page 19), but require some description. The furnace was erected on a separate stand quite independent of the measuring apparatus. It consisted of a narrow tube wound with a heating coil and containing, opposite the ends of the bar, two small openings through which the divisions could be seen. The inside diameter of the tube was 15 mm. and the side openings were narrow slits about 3 mm. in width by 10 mm. long. The tube and its heating coil extended 10 cm. beyond the ends of the bar and the wire was wound somewhat more closely at the ends than in the middle to counteract the cooling effect of the end and side openings. In this way a reasonably uniform distribution of temperature along the bar was secured.

The first furnace tube was of porcelain wound with nickel wire 1 mm. in diameter, the separate turns being insulated from each other with a mag-

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nesite cement which is sufficiently refractory and conducts but little at any temperature which the nickel wire can withstand. Thus arranged, the heating coil was mounted horizontally in a much larger tube (7.5 cm. diameter) of porcelain and the space between filled with dry calcined magnesia of good insulating quality. The whole was water-jacketed throughout in order to prevent any heat from the furnace from entering the optical system and disturbing the fixed distance between the micrometers, upon which the accuracy of the measurement absolutely depends. Both the insulating material and the water-jacket were provided with small openings corresponding to the slits in the furnace tube, so that the bar could be illuminated and observed from without.

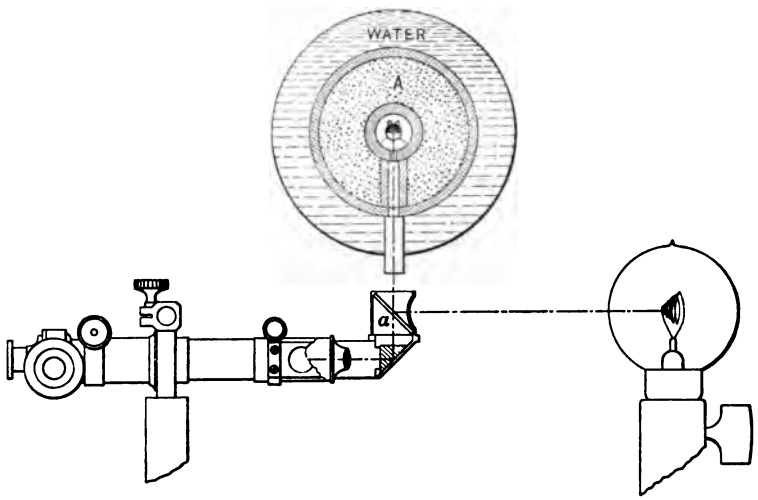


FIG. 6. A transverse section of the expansion-coefficient furnace (A) at one of the openings showing method of illumination by 45° plane glass plate (*a*). The bar and thermo-element appear in position, though not well shown by this section.

The measuring portion of the apparatus was entirely separate from the furnace and consisted of two telescopes, mounted upon upright brass tubes firmly secured in position upon massive brass carriages which slid freely on horizontal steel guide-bars, 25 mm. in diameter and ground true. The two carriages were then connected by an invar metal bar (Fig. 5), to which they were stoutly and permanently clamped. The whole system was then free to move upon its guides, but the relative position of the telescopes was fixed. The object of this arrangement was obviously to secure a constant distance between the telescopes, in spite of slight changes in the temperature of the system due to changes in the temperature of the room or to the heat from the observer's body, whatever the relative expansion of the various parts of the apparatus. After a good many observations had been made, it was found that the upright brass tubes supporting the telescopes upon their carriages were not uniformly affected by the heat from the body of the observer. They did not therefore expand uniformly and parallel to each other, but tended to buckle very slightly during each series of observations. This was subsequently corrected by a second invar bar above the telescopes, which in combination with the first formed a rugged rectangular

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system which preserved the cross-hair distance without change throughout long series of observations.

In mounting the furnace for observation, the side openings which gave access to the scale divisions were directed downward in order to reduce to a minimum the convection currents of air which endanger the constancy of the temperature within. The openings were also made as small as possible for the same reason. It therefore became something of a problem to bring in light enough to illuminate the scale divisions and at the same time to make observations of the change in length with the temperature. The device adopted was this: In the optical axes of the telescopes, and 3 to 4 cm. beyond the objective, small total reflecting prisms were mounted upon the extended telescope tubes in such a way as to deflect the line of sight at right angles and upward into the furnace. Above these prisms and between them and the furnace (see Fig. 6), windows of plane optical glass were set at 45° in such a way that they served to reflect the light from an incandescent lamp upward from their outer surfaces without materially interrupting the line of observation through the telescope and total reflecting prism. By this device the path of the illuminating light was the same as the path of the reflected light which reached the observer, which served to give plenty of illumination for the scale without increasing the size of the openings beyond what was required to see the actual expansion and to measure it.

The illumination was provided by a single incandescent lamp of 100 candle-power with a spiral filament of stock type giving an intense and concentrated illumination. It was mounted behind the furnace 15 cm. distant from the openings, and was so screened by circulating water that its heat did not reach the optical parts of the apparatus save in the two beams which entered the furnace for the illumination of the bar.

The temperature of the bar was determined at first with one thermo-element and afterward with two, which entered the furnace tube from opposite ends in such a way that their hot junctions could be bound together and moved freely along the bar and in contact with it, in order to give a double reading of the temperature at any point desired. In this way we obtained the actual distribution of temperature along the bar corresponding to each determination of its length.

To complete the system, a standard brass bar was prepared of the same size and shape as the platin-iridium bar under investigation, but with silver surfaces let in at the ends to carry the divisions. This bar was compared at 20° C. with the standards of length at the Bureau of Standards, and served to establish the absolute distance separating the cross-hairs before and after each set of observations.

The method of procedure was now substantially as follows: The standard brass bar was placed in position in the furnace at the temperature of the room. All of the necessary adjustments to secure good illumination, to bring the cross-hairs parallel to the scale divisions, and to bring the lines into sharp focus, were then made once for all, and these adjustments were never again disturbed until the series was completed. The field of the microscopes included 5 mm. of the bar, but only the three scale divisions bounding the 2 mm. nearest to the fixed cross-hair were used. Toward the close of the series, for an important reason which will presently appear,

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only the two bounding divisions of the single millimeter which included the fixed cross-hair were read and all the observations which had been made outside this limited region were rejected. Readings were made from left to right in each microscope and then repeated in the reverse direction to obviate errors from the micrometer screw. The temperature for this measurement was determined with mercury thermometers thrust into the ends of the furnace tube adjacent to the bar and read before and after the series of micrometer readings. This observation served to establish in absolute measure the distance apart of the fixed cross-hairs of the microscopes. The brass bar was then removed and the platin-iridium bar corresponding to the gas-thermometer bulb inserted in its place in the same relative position. It is necessary here again to emphasize the fact that all further adjustment must be made with the bar and not with the optical parts of the apparatus.

Having brought the bar into exactly the same position with respect to the telescopes which the brass bar previously occupied, and having introduced the thermo-elements in such a way that their hot junctions were free to travel along the bar from end to end without disturbing it, a second series of observations at the temperature of the room was made in the same way as before. This yielded the absolute length of the bar at room temperature in terms of the standard brass bar. The furnace was then ready for heating to the temperature desired.

In the determination of the high-temperature scale carried out at the Reichsanstalt in 1900, four observations of the expansion of the bulb material (250°, 500°, 750°, and 1000°) were deemed sufficient, and it was not thought necessary in our earlier observations to increase this number materially. We therefore began with a 200° interval. After the observation at the temperature of the room, the bar was accordingly heated to 200° C. and sufficient time (about 30 minutes) allowed for the temperature to become constant throughout the furnace, after which a temperature reading was made at the middle of the bar with each element. Observations of length were then made in the same order as before upon the pair of lines adjacent to the fixed cross-hair in each of the microscopes, followed by a second temperature reading at the middle of the bar. After these observations of length and before any change was made in the temperature, nine consecutive pairs of observations were made of the temperature distribution along the bar, first at the center, then on the left section at 5, 10, and 12 cm. out from the middle, then the center repeated; then upon the right section with similar intervals, and again the center, all with both elements. By this means an accurate measurement of the temperature along the bar corresponding to the length measurement just completed was obtained. The whole procedure was then repeated at temperatures of 400, 600, 800, and 1000° C.,[1] after which the furnace was allowed to cool over night and the length of the bar at the temperature of the room was again determined. Immediately following this, an observation of the brass bar was made in order to establish the fact that the distance separating the cross-hairs had not been accidentally disturbed by the manipulation of the furnace during heating.

[1]Subsequently, when we had reason to suspect an irregularity in the rate of expansion, these observations were repeated every 100° and then every 50° in the region between 600° and 1000°.

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At 800° and 1000° the bar is self-luminous to a sufficient extent to enable measurements to be readily made without outside light, but it was deemed advisable to use the outside light in the same way at these temperatures also. In passing from outside to inside illumination, the lines are at first dark on a bright ground, and then bright on a dark ground, a change to which the eye accustoms itself only with considerable difficulty. The measurements were therefore much more uniform when outside light was used throughout.

The measurements of the temperature at once encountered the difficulty that the exposure of the thermo-element in the presence of iridium at a temperature of 1000° contaminates it by an amount sufficient to cause a small but cumulative error. This exposure was necessary with the apparatus as we had arranged it, and there was therefore nothing to do but to make the time of the exposure as short as possible, and by the use of two elements fastened together and extending out of the furnace at opposite ends, to so arrange the conditions that any contamination, if sufficient to affect the temperature, would become immediately apparent. As W. P. White of this laboratory has shown in a recent paper,[1] the most critical portion of a thermo-element is not the portion along which the temperature is constant, but the region where the element passes from one temperature to another. In our furnace, for example, the region of exposure to constant temperature could give rise to no error of reading, however much the element might be contaminated in that region, but if a contaminated portion of the element were at any time to come into the region lying between the end of the bar and the outside of the furnace, an immediate difference in its reading should become evident.

It was therefore arranged that the junctions of two elements should be bound together so as to record the temperature of the same point within the furnace and, whenever this combination of two elements was moved toward one end of the bar or the other, that a greater length of one of the elements should be inside the furnace than of the other and a different section of wire be exposed in the transition zone. If there is contamination, a difference in reading between the two elements will then be immediately conspicuous. In the earlier observations comprising this investigation, only one element was used, and by way of control at the close of a long series of observations a second element was introduced in the manner indicated above. It then became immediately evident that the first element had become contaminated and that the observations made with it were affected to a degree which could not be established after the observations themselves were over, and which therefore necessitated the rejection of several entire series. This misfortune may serve to emphasize the necessity of using more than one thermo-element in all cases where it is possible to do so.

Three other difficulties were met with which proved to be sources of considerable inconvenience, and which serve in greater or less degree to place limits upon the accuracy attainable in this particular apparatus. The first was the temperature gradient along the bar, of which mention has already been made. Earlier observers have sometimes been content in similar cases to heat a bar with the electric furnace and to make their measurements upon cold projecting ends, that is, under conditions such that the actual temperature along the bar varies from the temperature of the room

[1] Walter P. White, Phys. Rev. 26, 535–536, 1908.

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to a maximum near the middle of the bar. The resulting temperature to which a given measured length is then referred is an integral of a temperature range which varies all the way from that of the room to some point considerably higher than that for which the length measurement is recorded.

This situation seems to us to comport badly with the accuracy otherwise attainable in measurements of this kind, if not to violate fundamental definitions. Unless the expansion coefficient can be treated as linear, such a determination is obviously only an approximation. Furthermore, there is ample precedent for anticipating inversions in an alloy of this character, such that the expansion coefficient of the material below the inversion temperature would differ considerably from that above it. An integration, therefore, in which the temperature range is large may well overlap two physical states in such a way that the length measurement loses all significance. We have not been able to establish the fact that such an inversion exists in the 10 per cent platin-iridium alloy within the temperature range over which these measurements were made, although there is a break in the continuity of the expansion, of small magnitude, which recurs with some persistence, as can be seen from the tables which follow (p. 36 et seq.).

Supposing such an inversion to exist, it would of course follow that the expansion would be a discontinuous function of the temperature, a separate expansion coefficient would need to be determined above and below this point, and the two would not bear any necessary relation to each other. If such a situation exists in the present bar, the difference is so small as to be negligible for our present purpose, but the plain indication of an irregularity led us to appreciate the necessity of maintaining the bar as nearly constant in temperature as possible during the length measurements in order to enable us to interpret the measurements intelligently.

The problem of accomplishing this result gave us considerable anxiety. As has been stated above, the scheme of making optical measurements directly upon the bar without multiplying device of any kind necessarily involves an opening in the furnace coil opposite each end of the bar, and a consequent cooling of that portion of the bar which is opposite the opening. The amount of this cooling, which is greatest at the highest temperatures, reached a value of about 4 per cent in the first furnace coil which we wound. The temperature distribution along the bar is measurable with any accuracy desired by moving the thermo-elements about, or its effective average can be determined by direct integration with a platinum resistance thermometer of equal length, stretched parallel to the bar. We chose the former method on the ground that it yielded more information, and then sought in addition to diminish the irregularity as much as possible for the reason given above. Accordingly, another furnace coil was wound with the turns closer together near the openings. This changed the temperature gradient considerably without materially improving it (see Furnace II, seq.), after which a third coil was prepared with still closer windings, which proved to be considerably overcompensated and was rejected.

In all we made five separate trials of this kind, in the last two of which (Furnaces III and IV) a thick-walled iron tube was substituted for the porcelain furnace tube in the hope of gaining increased uniformity of temperature through the increased heat conductivity of the tube itself. This arrangement succeeded better, but we found it impossible to so arrange a winding

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that the temperature opposite the openings was uniform with that at the middle of the tube for all temperatures between 0 and 1000°.[1] A winding which gave good results at the lower temperatures gave insufficient compensation at the higher ones. The obvious possibility of reaching a uniform distribution, by subdividing the coil into sections in each of which the current could be independently varied was not tried on account of the cumbersome manipulation required, and in part also because the results which we obtained with considerable differences in the gradient appeared to agree very well among themselves.

The temperature carried out in the tables in each case represents the integral of the nine pairs of readings described above. The actual error which enters into an observation from the variation in temperature opposite the openings is therefore the error in establishing this integral, which can hardly be greater than 1° C. or 0.1 per cent.

It will probably occur to other experimenters, as it did to us, that this difficulty with the exposed ends of the bar is due in part to the unavoidable air-currents circulating through the small openings, and that these ought to be checked by the introduction of windows. We made two attempts to reach the difficulty in this way, first using quartz windows set in the opening of the furnace tube itself and therefore heated with the tube; and second, by the use of glass windows set in the water-jacket and therefore outside of the heated zone. The quartz windows behaved very well until high temperatures were reached, when they became displaced by the unequal expansions in the apparatus, thereby causing displacements in the apparent position of the lines of the scale. When the windows were removed to the colder parts of the furnace in order to avoid this displacement, sufficient water-vapor condensed upon them from within to obscure the field, so that the window scheme had to be entirely abandoned.

The second considerable difficulty to be encountered was due to the effect of the outside illumination of the divisions of the bar in a rather highly magnified field (about 25 diameters). Consider the bar to be illuminated by a beam of light from a fixed source which remains constant in position while the bar expands, and the light received through the telescope into the eye to be reflected from the polished parts of the bar surface between the rulings. For reasons which appear in Fig. 7, this reflected light does not show the lines to be equally[2] displaced after expansion. The reason for this is plain after a brief consideration. If lines are ruled with a sharp tool upon soft platinum metal which is afterwards polished to remove the burr left by the cutting tool, the effect is to round off the two edges of each cut to a greater or less extent, and thereby to present approximately cylindrical bounding surfaces to the incident light. The apparent boundary of the line will then be defined by the reflection of this light from the cylindrical surface into the telescope. Now, if this cylinder be moved laterally in the direction produced by the expansion, the light will be reflected from a different point on the cylinder and will therefore show the line in a somewhat different apparent position from that which would be produced by

[1] A considerable part of the difficulty in correcting the irregular furnace temperature was due to the instability of nickel wire at the higher temperatures. The oxidation is so rapid that a favorable arrangement of the windings, when obtained, does not give uniform results for more than one or two series of observations. It was subsequently abandoned in favor of pure platinum.

[2] The small expansions of the millimeter sections themselves have been taken into account, although not explicitly mentioned in this discussion.

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the expansion alone. The drawing is purposely exaggerated to show exactly the character of this optical error.

It was our habit in beginning these observations to select three appropriate lines upon each end of the bar, and to make all the measurements on these, whereupon it was found by a careful examination of the results that the displacement of the three lines after expansion differed systematically by a measurable amount and in a manner which could not be accounted for by the movement of the bar. This difference was very puzzling for a long time, but was finally traced to the source described, and this inference verified by actually moving the bar about in the field in various ways without changing the temperature. The consequence of this discovery was to compel the rejection of all measurements made upon lines other than those immediately adjacent to the fixed cross-hair in the center of the field. The number of observations at each end was therefore reduced to two, but the agreement of the results was very considerably increased thereby.

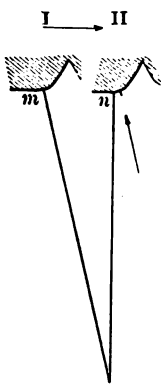


FIG. 7. Showing how the lines appeared displaced after expansion. Actual expansion, *m* to point indicated by the arrow. Apparent expansion, *m* to *n*.

The third difficulty is a limitation of the material itself and is therefore not dependent upon the method of measurement. It is the failure of the bar to return to its initial length after heating.

In this particular bar, 25 cm. in length, we actually found differences between the lengths before and after heating of the order of magnitude of 0.02 mm., which varied from one series of experiments to another according as the bar happened to be cooled rapidly or slowly. This quantity is some fifty times larger than the smallest magnitude we could measure, and inasmuch as it depends only upon measurements at the temperature of the room is readily accessible. This limitation of platin-iridium is not sufficient to deprive it of continued usefulness for the gas thermometer. It is the contaminating action of the iridium which distils out of the alloy at all temperatures above 900° in sufficient quantities to eventually destroy the accuracy of the thermo-element, that has led us to abandon the iridium alloy for an alloy of rhodium (see p. 50).

This study of the irregularities present or possible in the expansion of the bulb was pursued much more persistently than is usual in an investigation which is but incidental to a much larger one, on account of the unexpected values obtained. The expansion of pure platinum as determined by Holborn and Day[1] is given by the equation

$$\lambda = (8868t + 1.324t^2)\ 10^{-9}$$

while that of platinum, containing 20 per cent of iridium, made in the same furnace gave

$$\lambda = (8198t + 1.418\ t^2)\ 10^{-9}$$

We had expected, as Holborn and Day assumed in their calculations in 1900, that the expansion of the 10 per cent alloy ought to fall approximately between the two. When it therefore became apparent that our observations were leading to a value, for the 10 per cent alloy, which was of the same

[1] On the expansion of certain metals at high temperatures, Am. Jour. Sci. (4), 11, 374-390, 1901. Ann. d. phys. (4), 4, 104-122, 1901.

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order of magnitude as that hitherto found for pure platinum, we were for a long time quite unwilling to accept the result. After the close scrutiny of the apparatus and its limitations described above, all of which, either singly or in combination, appeared totally inadequate to account for the unexpected expansion coefficient obtained, there remained the single possibility that some confusion had arisen in the preparation of the bar; but Doctor Heraeus, who made the bar, would not admit this possibility. Even then, it was deemed wise to make a chemical analysis of the bar itself, and this was done by E. T. Allen of this laboratory, with the result that the iridium content was found to be 10.6 per cent. There appears therefore no further alternative but to accept the irregular variation of the expansion with the percentage composition as characteristic of platin-iridium, following the well-known example of the iron-nickel alloys.

## EXPERIMENTAL DATA.

TABLE I.—OBSERVATIONS ON THE EXPANSION COEFFICIENT OF THE ALLOY 90 PT. 10 IR.

In Furnace I: Temperature distribution along the bar.

| Left. | | | Middle. | Right. | | |
|---|---|---|---|---|---|---|
| 12 cm. | 10 cm. | 5 cm. | (Corrected temperature.) | 5 cm. | 10 cm. | 12 cm. |
| +10° | +11° | + 7° | 287.7° | − 4° | −13° | −15° |
| +12 | +13 | + 7 | 511.2 | − 2 | −15 | −24 |
| +10 | +23 | +13 | 700. | − 5 | −21 | −30 |
| +28 | +33 | +17 | 1044.1 | −11 | −31 | −46 |

In Furnace I: Expansion.

$\lambda = \frac{l}{L} = \frac{\text{total expansion}}{\text{initial length}}$

Equation used for the "calculated" expansions, $\lambda = (8869.5t + 1.3192t^2)10^{-9}$

| Date. | Corrected temperature. | λ | | Obs.—Cal |
|---|---|---|---|---|
| | | Observed. | Calculated. | |
| December 30, 1907..... | [1]287.7° | .002635 | .002661 | −26 |
| | 511.2 | .004871 | .004879 | − 8 |
| | 712.9 | .007051 | .006994 | +57 |
| December 31, 1907..... | 700.0 | .006878 | .006855 | +23 |
| | 866.6 | .008653 | .008677 | −24 |
| January 2, 1908..... | 504.0 | .004812 | .004805 | + 7 |
| | 504.4 | .004813 | .004810 | + 3 |
| | 690.0 | .006763 | .006748 | +15 |
| | 689.4 | .006755 | .006742 | +13 |
| | 856.5 | .008600 | .008565 | +35 |
| | 856.4 | .008610 | .008564 | +46 |
| | 1044.1 | .010616 | .010699 | −83 |
| | 1043.8 | .010635 | .010695 | −60 |

[1]Inasmuch as the expansion-coefficient which is here being determined itself enters into the determination of the temperature, the two quantities are not independently variable. The temperatures given above are therefore based upon tentatively assumed constants which have been chosen about where the final values were expected to come. The assumed data are these: melting-point of zinc, 419°; of silver, 960°; of copper, 1083°. With actual temperatures 1° higher or lower, the expansion coefficient would not be affected by an amount equal to one-tenth of one per cent in any part of the curve. The assumed values are, therefore, amply exact for the purpose.

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TABLE I—Continued.

In Furnace II: Temperature distribution along the bar.

| Left. | | | Middle. | Right. | | |
|---|---|---|---|---|---|---|
| 12 cm. | 10 cm. | 5 cm. | (Corrected temperature.) | 5 cm. | 10 cm. | 12 cm. |
| −13° | − 1° | 0° | 294.0° | −4° | −12° | −27° |
| −22 | − 6 | − 2 | 392.0 | −6 | −20 | −41 |
| −28 | − 9 | − 4 | 491.0 | +2 | −17 | −33 |
| −30 | −13 | − 5 | 592.5 | 0 | −10 | −30 |
| −34 | −15 | − 5 | 695.0 | +4 | − 3 | −27 |
| −35 | −17 | − 7 | 795.0 | +8 | + 4 | −17 |
| −52 | −21 | − 9 | 894.0 | +9 | + 6 | −12 |
| −51 | −21 | −10 | 994.0 | +8 | + 8 | −14 |

In Furnace II: Expansion.

Equation used for the "calculated" expansions, $\lambda = (8778.6t + 1.2801t^2)10^{-9}$

| Date. | Corrected temperature. | λ | | Obs.—Cal. |
|---|---|---|---|---|
| | | Observed. | Calculated. | |
| February 25, 1908..... | 294.0° | .002679 | .002692 | −13 |
| | 392.0 | .003665 | .003638 | +27 |
| | 491.0 | .004660 | .004619 | +41 |
| | 592.5 | .005632 | .005651 | −19 |
| | 695.0 | .006657 | .006719 | −62 |
| | 795.0 | .007741 | .007788 | −47 |
| | 894.0 | .008848 | .008871 | −23 |
| | 994.0 | .010086 | .009991 | +95 |

In Furnace III: Temperature distribution along the bar.

| Left. | | | Middle. | Right. | | |
|---|---|---|---|---|---|---|
| 12 cm. | 10 cm. | 5 cm. | (Corrected temperature.) | 5 cm. | 10 cm. | 12 cm. |
| − 2° | − 1° | 0° | 297.9° | − 1° | − 5° | − 7° |
| − 6 | − 3 | −1 | 397.3 | − 1 | − 5 | − 8 |
| − 9 | − 6 | −2 | 496.3 | − 1 | − 5 | − 9 |
| −13 | −10 | −3 | 594.3 | + 1 | − 3 | − 7 |
| −16 | −12 | −4 | 646.9 | + 2 | − 2 | − 6 |
| −16 | −12 | −4 | 646.6 | + 2 | − 2 | − 5 |
| −17 | −13 | −4 | 697.0 | + 2 | 0 | − 4 |
| −19 | −14 | −5 | 747.8 | + 4 | + 2 | − 2 |
| −23 | −17 | −6 | 796.3 | + 5 | + 3 | 0 |
| −27 | −20 | −7 | 846.2 | + 6 | + 5 | + 1 |
| −26 | −20 | −8 | 897.2 | + 6 | + 8 | + 4 |
| −29 | −23 | −9 | 946.6 | + 7 | +11 | + 8 |
| −31 | −25 | −9 | 1001.5 | +11 | +17 | +14 |

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TABLE I—Continued.

In Furnace III: Expansion.

Equation used for the "calculated" expansions, $\lambda = (8874.4t + 1.2889t^2)10^{-9}$

| Date. | Corrected temperature. | $\lambda$ | | Obs.—Cal. |
|---|---|---|---|---|
| | | Observed. | Calculated. | |
| April 6, 1908..... | 297.9° | .002770 | .002759 | +11 |
| | 397.3 | .003739 | .003730 | + 9 |
| | 496.3 | .004720 | .004723 | − 3 |
| | 594.3 | .005714 | .005732 | −18 |
| | 646.9 | .006267 | .006283 | −16 |
| | 646.6 | .006262 | .006280 | −18 |
| April 8, 1908..... | 697.0 | .006800 | .006815 | −15 |
| | 747.8 | .007346 | .007360 | −14 |
| | 796.3 | .007897 | .007888 | + 9 |
| | 846.2 | .008445 | .008437 | + 8 |
| | 897.2 | .009013 | .009005 | + 8 |
| | 946.6 | .009579 | .009561 | +18 |
| | 1001.5 | .010206 | .010187 | +19 |

In Furnace IV: Temperature distribution along the bar.

| Left. | | | Middle. (Corrected temperature.) | Right. | | |
|---|---|---|---|---|---|---|
| 12 cm. | 10 cm. | 5 cm. | | 5 cm. | 10 cm. | 12 cm. |
| − 3° | − 2° | 0° | 299.1° | − 1° | − 4° | − 5° |
| − 5 | − 3 | 0 | 399.2 | − 1 | − 4 | − 6 |
| − 9 | − 5 | − 1 | 497.0 | − 1 | − 5 | − 7 |
| −14 | − 9 | − 2 | 598.3 | 0 | − 3 | − 6 |
| −16 | − 9 | − 3 | 648.0 | + 1 | − 1 | − 5 |
| −19 | −12 | − 4 | 709.5 | + 3 | 0 | − 4 |
| −21 | −15 | − 4 | 748.7 | + 4 | + 2 | − 3 |
| −25 | −18 | − 6 | 799.1 | + 6 | + 4 | − 1 |
| −30 | −22 | − 7 | 846.1 | + 7 | + 6 | + 1 |
| −30 | −22 | − 8 | 900.4 | + 8 | + 9 | + 4 |
| −36 | −26 | −10 | 949.6 | +10 | +13 | + 7 |
| −36 | −27 | −11 | 1000.5 | +12 | +17 | +11 |

In Furnace IV: Expansion.

Equation used for the "calculated" expansions, $\lambda = (8814.1t + 1.3260t^2)10^{-9}$

| Date. | Corrected temperature. | $\lambda$ | | Obs.—Cal. |
|---|---|---|---|---|
| | | Observed. | Calculated. | |
| April 17, 1908..... | 299.1° | .002763 | .002755 | + 8 |
| | 399.2 | .003750 | .003730 | +20 |
| | 497.0 | .004697 | .004708 | −11 |
| | 598.3 | .005702 | .005748 | −46 |
| | 648.0 | .006265 | .006268 | − 3 |
| | 709.5 | .006889 | .006921 | −32 |
| | 748.7 | .007344 | .007343 | + 1 |
| | 799.1 | .007897 | .007890 | + 7 |
| | 846.1 | .008423 | .008407 | +16 |
| | 900.4 | .009018 | .009011 | + 7 |
| | 949.6 | .009585 | .009566 | +19 |
| | 1000.5 | .010160 | .010146 | +14 |

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The mean of the equations derived from the observations in the four furnaces, each weighted according to the number of observations in that particular series, is

$$\lambda = (8841t + 1.306t^2)\ 10^{-9}$$

which is the equation used to compute all the gas-thermometer observations made with the platin-iridium bulb.

This interpolation formula is a simple equation of two coefficients obtained by the method of least squares, giving equal weight to all the observations.

Inasmuch as no one of the differences between observed and calculated values reaches 1 per cent in value, this form of equation, which has been frequently employed for the purpose, is perhaps as well adapted to represent the experimental data as another. When it was discovered that the bar after heating did not return to its initial length, but varied within considerable limits from one heating to another, it became apparent that if the contraction upon cooling was not uniform, the expansion on reheating was probably also irregular to the same degree, and that the room temperature observations could not be expected to follow this or any other simple equation very consistently. That such irregularities exist and attain such magnitude as seriously to limit the power of any simple formula to reproduce the expansions over the whole range will be immediately apparent from an examination of the columns of differences (Obs.—Cal.). It is more directly observable in the experimentally determined values of the expansion between 0 and 300° taken from the four series which have just been given.

MEASURED EXPANSION IN MILLIMETERS BETWEEN 0° AND 300°.

| | |
|---|---|
| December 30, 1907 | 0.687 |
| February 25, 1908 | 0.681 |
| April 6, 1908 | 0.700 |
| April 17, 1908 | 0.696 |

By way of experiment we tried an equation of three coefficients on the last two series, both of which contain observations at 50° intervals, omitting in each case the room temperature observation in which the irregularity in the expansion itself chiefly appears, and found it possible to reproduce the measured behavior of the bar in the region from 300° to 1000° with differences less than one-fifth as large as those recorded in the tables above. There is, therefore, abundant evidence that the uncertain region is confined to the lower temperatures and that the higher temperatures have so far offered no serious difficulty or irregularity, either in measurement or convenient representation. The expansion measurements over the entire range from 0° to 1000° may be in error by about 0.5 per cent, most of which is directly attributable to these irregularities in the behavior of the metal at the lower temperatures. In the gas thermometer this corresponds to about 0.25° at 1000°.

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## 8. THE PRESSURE COEFFICIENT OF NITROGEN.

A number of determinations of the pressure coefficient of nitrogen, under different initial pressures, were made by observing the pressure inside the bulb when it was immersed alternately in ice and in steam, with the following results. Values of $\alpha$ obtained by Chappuis are also given.

| Day and Clement. | | | Chappuis.[1] | |
|---|---|---|---|---|
| No. of observations. | Initial pressure. | $\alpha$ | Initial pressure. | $\alpha$ |
| 4 | 314 mm. | 0.003665 | 528.8 mm. | 0.00366811 |
| 5 | 550 | .003668 | 534.3 | .00366846 |
| 6 | 744 | .003670 | 793.5 | .00367180 |
| 12 | 985 | .003673 | 995.9 | .00367466 |

## 9. GAS-THERMOMETER MEASUREMENTS. FIRST SERIES.

### COMPUTATION OF RESULTS.

The following formula for the constant-volume gas thermometer was used for the computation of results obtained with the platin-iridium bulb:

$$\frac{pV}{1+\alpha t}+\frac{pv_1}{1+\alpha t_1}+\frac{pv_2}{1+\alpha t_2}=p_0V_0+\frac{p_0v_1}{1+\alpha t'_1}+\frac{p_0v_2}{1+\alpha t'_2}$$

In this equation:

$V_0$ = volume of bulb at 0°..... 195.547 cc.
$V$ = volume of bulb at $t$.°
$p_0$ = initial pressure, i. e., pressure when bulb is at 0°.
$p$ = pressure at temperature of $t$°.
$v_1$ = portion of "unheated space" inclosed in furnace (in which temperature varies from the temperature of the bulb to that of the room)..... 0.161 cc.
$v_2$ = portion of "unheated space" outside of furnace..... 0.128 cc.
$t_1$ = estimated mean temperature of $v_1$ when bulb is at $t$°.
$t'_1$ = estimated mean temperature of $v_1$ when bulb is at 0°.
$t_2$ = temperature of $v_2$ when bulb is at $t$°.
$t'_2$ = temperature of $v_2$ when bulb is at 0°.
$\alpha$ = expansion coefficient of nitrogen under constant volume.
$\beta$ = linear coefficient of expansion of platinum-iridium alloy.

Writing $A=\frac{v_1/V_0}{1+\alpha t'_1}+\frac{v_2/V_0}{1+\alpha t'_2}$ and $B=\frac{v_1/V_0}{1+\alpha t_1}+\frac{v_2/V_0}{1+\alpha t_2}$

the equation may be transformed into a more convenient form for computation:

$$1+\alpha t=\frac{p}{p_0}\,\frac{1+3\beta t}{1+A-\frac{p}{p_0}B}$$

$3\beta t$ represents the correction for the expansion of the bulb and $A-\frac{p}{p_0}B$ is the correction for the unheated space. In computing $p$ the mercury columns were corrected in the usual manner for temperature and latitude.

[1] Travaux et Mémoires du Bureau International des Poids et Mesures, vols. 6 and 12, 1888 and 1902.

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## EXPERIMENTAL DATA.

Table II contains some of the earlier results, which were obtained after the temperature gradient along the bulb had been only partially corrected. During this series of observations, the temperature difference between the middle and either end of the bulb varied between 50 and 150 microvolts (5° to 15°). As it was impossible entirely to eliminate the gradient with the arrangement of coils in use at this time, the heating currents were adjusted so as to have the gradients toward the top and bottom of the bulb of opposite sign and of nearly equal value, thereby materially reducing the magnitude of the correction to be applied.

TABLE II.

Initial pressure, 302.3 mm. $\alpha = 0.003665$.
Average temperature difference between middle and either end of bulb, 10°.
Equation used for "calculated" temperatures,

$$t = 50.19 + 0.11176\, e - 1.289 \times 10^{-6} e^2.$$

| 1906. | $p_0$ | Thermo-couple P. | Temperature observed. | Temperature calculated. | $t$ (obs.)—$t$ (cal.) |
|---|---|---|---|---|---|
| | *mm.* | *mv.* | | | |
| April 30.. | 302.09 | 3231.[1] | 396.8° | 397.8° | −1.0° |
| | | 4738. | 550.4 | 550.8 | − .4 |
| | | 6232. | 696.5 | 696.6 | − .1 |
| | | 7302. | 797.6 | 797.5 | + .1 |
| | | 8428. | 900.2 | 900.5 | − .3 |
| | | 9547. | 998.4 | 999.6 | −1.2 |
| | | 11004. | 1123.5 | 1123.9 | − .4 |
| May 1.... | 302.20 | | | | |
| May 2..... | | 2961.[1] | 368.6 | 369.8 | −1.2 |
| | | 4944. | 571.2 | 571.2 | .0 |
| | | 6448. | 717.8 | 717.2 | + .6 |
| | | 7525. | 818.6 | 818.2 | + .4 |
| | | 8094. | 869.7 | 870.3 | − .6 |
| | | 9040. | 954.5 | 955.1 | − .6 |
| | | 9750. | 1016.4 | 1017.3 | − .9 |
| | | 10583.[2] | 1089.9 | 1188.5 | +1.4 |
| May 3... | 302.29 | | | | |
| May 4..... | | 3928. | 470.0 | 469.3 | + .7 |
| | | 5186. | 595.2 | 595.1 | + .2 |
| | | 5944. | 669.1 | 668.9 | + .2 |
| | | 6725. | 743.8 | 743.4 | + .4 |
| | | 7755. | 839.7 | 839.3 | + .4 |
| | | 9255 | 973.1 | 974.1 | −1.0 |
| | | 10135. | 1049.9 | 1050.4 | − .5 |
| May 5... | 302.30 | | | | |
| May 7..... | | 3918. | 468.0 | 468.3 | − .3 |
| | | 6926. | 762.8 | 762.4 | + .4 |
| | | 8910. | 943.4 | 943.6 | − .2 |
| | | 10631. | 1092.8 | 1092.6 | + .2 |
| | | 11264. | 1147.0 | 1145.4 | +1.6 |
| May 9... | 302.52 | | | | |

Before beginning this series of observations and again after its completion, the thermo-couple $P$ was calibrated by determining its electromotive force at the zinc and copper melting-points. From the results which follow it will

[1] Observations below 400° were not used in computing the parabola.
[2] Temperature fell 2° during observation.

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be seen that the electromotive force of the thermo-element, at the temperature of melting copper, has been lowered 15 microvolts (1.2°) through iridium contamination during the series of measurements:

| | | Zinc. | | Copper. | |
|---|---|---|---|---|---|
| April 28, 1906 | F.[1] | 3398 | | 10488 | |
| | M | 3398 | | 10483 | |
| | | | 3398 | | 10486 |
| May 14, 1906 | F | 3396 | | 10469 | |
| | M | 3398 | | 10472 | |
| | | | 3397 | | 10471 |

After these observations (Table II) the furnace was rebuilt. In place of the heating coil of platinum-iridium alloy, a coil of pure platinum was substituted. At the same time the arrangement of the two auxiliary heating coils was so modified that by proper adjustment of rheostats, the gradient along the bulb could be reduced to 0.5° or less.

Table III contains a complete series of 76 observations, without omission, covering a period of more than three months in time, in the order in which they were made and with the control melting-points through which the constancy of the thermo-elements was assured.

In order to eliminate, as far as possible, any error due to the contamination of the thermo-couples with iridium, the couples were calibrated from time to time by metal melting-point determinations. Columns 7 to 10 of Table III contain the E. M. F's of the standard thermo-couple *W* for these calibrations.

As a check against accidental errors of observation, all observations were made in pairs, with an interval of from 5 to 10 minutes between.

In computing the constants of the equation

$$e = -305.5 + 8.1749t + 0.001654t^2$$

which was used for the "calculated" electromotive forces, the observations marked * in Table III were omitted in order to equalize the intervals between points. By comparing the values $t$ (obs.) $-t$ (calc.) (Table III) of the various pairs of observations, it will be seen that any two determinations at the same temperature agree within 0.1°. The differences between observed and calculated temperatures are all considerably less than 1°. The greatest difference is 0.6°, and the average difference 0.2°.

If we now regroup these observations (Table IV) in the order of increasing temperatures and combine the pairs referred to above, the relation between the observed and calculated curves appears in a most favorable light. The average difference in column 6, Table IV, is even smaller than in Table III and wholly free from systematic variation.[2]

[1] F = Freezing-point, M = Melting-point.

[2] When these observations were first published (Am. Jour. Sci. (4), **26**, 405-463, 1908), the "calculated" values were obtained from the equation

$$t = 51.72 + 0.112499\,e - 1.35512 \times 10^{-6}\,e^2$$

and showed systematic variations from the observed temperatures amounting in maximum to 0.7°. This was interpreted to mean that the simple parabola was no longer adequate to represent the observations with sufficient accuracy. In a private letter Dr. George F. Becker subsequently called the attention of the authors to the fact that if the least-square solution were computed with $e$ expressed in terms of $t$ these systematic differences not only disappeared but a much better agreement (obs.−calc.) was obtained. Tables III, IV, and V have accordingly been recomputed with Dr. Becker's equation, with the result that the grounds for apprehension expressed in the previous paper have happily disappeared.

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TABLE III.

All electromotive forces are expressed in terms of thermo-element *W*. Initial pressure 287.5 mm. $\alpha = 0.003665$. Maximum temperature difference between middle and either end of bulb 0.5°. Equation used for "calculated" electromotive forces:

$$e = -305.5 + 8.1749t + 0.001654t^2.$$

| No. | Date. | Initial pressure in bulb. ($p_0$) | Observed temperature gas thermometer. | Observed electromotive force. Element *W*. | Calculated electromotive force. | Obs.−Calc. | Obs.−Calc. | Constancy of standard thermo-element (*W*) in terms of metal melting-points. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Zinc. | Silver. | Gold. | Copper. |
| | 1907. | | ° | *mv.* | *mv.* | *mv.* | ° | *mv.* | *mv.* | *mv.* | *mv.* |
| | Feb. 4 | ..... | ..... | ..... | ..... | ..... | ..... | 3403 | ..... | ..... | ..... |
| | Mar. 6 | 287.55 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 1 | 6 | ..... | 414.49 | 3367. | 3367.1 | −0.1 | 0.0 | ..... | ..... | ..... | ..... |
| 2 | 6 | ..... | 414.96 | 3371. | 3371.5 | −0.5 | −0.1 | ..... | ..... | ..... | ..... |
| 3 | 6 | ..... | 431.76 | 3532.* | 3532.4 | −0.4 | 0.0 | ..... | ..... | ..... | ..... |
| 4 | 6 | ..... | 432.25 | 3536.* | 3537.1 | −1.1 | −0.1 | ..... | ..... | ..... | ..... |
| | 6 | 287.39 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 5 | 7 | ..... | 419.96 | 3416. | 3419.3 | −3.3 | −0.3 | ..... | ..... | ..... | ..... |
| 6 | 7 | ..... | 420.00 | 3417. | 3419.7 | −2.7 | −0.3 | ..... | ..... | ..... | ..... |
| 7 | 7 | ..... | 436.23 | 3571.* | 3575.4 | −4.4 | −0.5 | ..... | ..... | ..... | ..... |
| 8 | 7 | ..... | 436.40 | 3574.* | 3577.0 | −3.0 | −0.3 | ..... | ..... | ..... | ..... |
| 9 | 7 | ..... | 458.55 | 3789.* | 3790.9 | −1.9 | −0.2 | ..... | ..... | ..... | ..... |
| 10 | 7 | ..... | 458.94 | 3793.* | 3794.6 | −1.6 | −0.2 | ..... | ..... | ..... | ..... |
| | 9 | 287.34 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 11 | 12 | ..... | 408.51 | 3309.* | 3310.0 | −1.0 | −0.1 | ..... | ..... | ..... | ..... |
| 12 | 12 | ..... | 408.71 | 3310.* | 3312.0 | −2.0 | −0.2 | ..... | ..... | ..... | ..... |
| 13 | 12 | ..... | 421.50 | 3430. | 3434.1 | −4.1 | −0.4 | ..... | ..... | ..... | ..... |
| 14 | 12 | ..... | 421.50 | 3429. | 3434.1 | −5.1 | −0.5 | ..... | ..... | ..... | ..... |
| 15 | 12 | ..... | 432.83 | 3540.* | 3542.7 | −2.7 | −0.3 | ..... | ..... | ..... | ..... |
| 16 | 12 | ..... | 432.89 | 3540.* | 3543.3 | −3.3 | −0.3 | ..... | ..... | ..... | ..... |
| | 13 | 287.35 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| | 14 | ..... | ..... | ..... | ..... | ..... | ..... | F 3405 | ..... | ..... | 10461 |
| | | | | | | | | M3404 | | | 10461 |
| | 14 | 287.35 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 17 | 15 | ..... | 1078.02 | 10430.5 | 10429.1 | +1.4 | +0.1 | ..... | ..... | ..... | ..... |
| 18 | 15 | ..... | 1077.05 | 10419. | 10417.7 | +1.3 | +0.1 | ..... | ..... | ..... | ..... |
| | 15 | 287.39 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| | 16 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 10463 |
| | | | | | | | | | | | 10462 |
| 19 | 20 | ..... | 1013.17 | 9671. | 9674.7 | −3.7 | −0.3 | ..... | ..... | ..... | ..... |
| 20 | 20 | ..... | 1012.43 | 9664. | 9666.1 | −2.1 | −0.2 | ..... | ..... | ..... | ..... |
| 21 | 20 | ..... | 1079.96 | 10446. | 10451.8 | −5.8 | −0.5 | ..... | ..... | ..... | ..... |
| 22 | 20 | ..... | 1078.26 | 10426. | 10431.9 | −5.9 | −0.5 | ..... | ..... | ..... | ..... |
| 23 | 20 | ..... | 1079.02 | 10434. | 10440.8 | −6.8 | −0.6 | ..... | ..... | ..... | ..... |
| 24 | 20 | ..... | 1032.75 | 9895.5 | 9901.0 | −5.5 | −0.5 | ..... | ..... | ..... | ..... |
| 25 | 20 | ..... | 1032.70 | 9895. | 9900.4 | −5.4 | −0.5 | ..... | ..... | ..... | ..... |
| | 21–22 | ..... | ..... | ..... | ..... | ..... | ..... | F 3405 | ..... | ..... | 10457 |
| | | | | | | | | M3405 | | | 10456 |
| | 23 | 287.55 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| | Apr. 2–3 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | F9046 | 10214 | 10454 |
| | | | | | | | | | 9046 | 10214 | 10454 |
| | 22 | 287.51 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 26 | 23 | ..... | 416.14 | 3383. | 3382.8 | +0.2 | 0.0 | ..... | ..... | ..... | ..... |
| 27 | 23 | ..... | 416.26 | 3384. | 3384.0 | 0.0 | 0.0 | ..... | ..... | ..... | ..... |
| 28 | 23 | ..... | 520.07 | 4393. | 4393.3 | −0.3 | 0.0 | ..... | ..... | ..... | ..... |
| 29 | 23 | ..... | 519.71 | 4388. | 4389.8 | −1.8 | −0.2 | ..... | ..... | ..... | ..... |
| 30 | 24 | ..... | 489.79 | 4095. | 4095.2 | −0.2 | 0.0 | ..... | ..... | ..... | ..... |
| 31 | 24 | ..... | 489.89 | 4097. | 4096.2 | +0.8 | +0.1 | ..... | ..... | ..... | ..... |
| 32 | 24 | ..... | 588.00 | 5073.5 | 5073.1 | +0.4 | 0.0 | ..... | ..... | ..... | ..... |
| 33 | 24 | ..... | 587.97 | 5072.5 | 5072.8 | −0.3 | 0.0 | ..... | ..... | ..... | ..... |

*In computing the constants of the equation at the head of Table III, the observations marked * were omitted in order to equalize the intervals between points.

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TABLE III—Continued.

| No. | Date. | Initial pressure in bulb. ($p_0$) | Observed temperature gas thermometer. | Observed electromotive force. Element $W$. | Calculated electromotive force. | Obs.—Calc. | Obs.—Calc. | Constancy of standard thermoelement ($W$) in terms of metal melting-points. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Zinc. | Silver. | Gold. | Copper. |
| | 1907. | | ° | *mv.* | *mv.* | *mv.* | ° | *mv.* | *mv.* | *mv.* | *mv.* |
| 34 | Apr. 24 | ..... | 688.44 | 6104. | 6106.2 | −2.2 | −0.2 | ..... | ..... | ..... | ..... |
| 35 | 24 | ..... | 687.84 | 6099.5 | 6100.0 | −0.5 | 0.0 | ..... | ..... | ..... | ..... |
| | 25 | 287.56 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 36 | 26 | ..... | 550.81 | 4700.5 | 4699.1 | +1.4 | 0.1 | ..... | ..... | ..... | ..... |
| 37 | 26 | ..... | 550.65 | 4698. | 4697.5 | +0.5 | 0.0 | ..... | ..... | ..... | ..... |
| 38 | 26 | ..... | 769.49 | 6962. | 6964.2 | −2.2 | −0.2 | ..... | ..... | ..... | ..... |
| 39 | 26 | ..... | 768.86 | 6957.5 | 6957.5 | 0.0 | 0.0 | ..... | ..... | ..... | ..... |
| 40 | 26 | ..... | 866.45 | 8020.5 | 8019.2 | +1.3 | +0.1 | ..... | ..... | ..... | ..... |
| 41 | 26 | ..... | 867.99 | 8029. | 8036.2 | −7.2 | −0.6 | ..... | ..... | ..... | ..... |
| 42 | 27 | ..... | 644.34 | 5648. | 5648.5 | −0.5 | −0.1 | ..... | ..... | ..... | ..... |
| 43 | 27 | ..... | 644.24 | 5646. | 5647.5 | −1.5 | −0.1 | ..... | ..... | ..... | ..... |
| 44 | 27 | ..... | 957.20 | 9036. | 9034.8 | +1.2 | +0.1 | ..... | ..... | ..... | ..... |
| 45 | 27 | ..... | 958.81 | 9054. | 9053.0 | +1.0 | +0.1 | ..... | ..... | ..... | ..... |
| 46 | 29 | ..... | 451.00 | 3718. | 3717.8 | +0.2 | 0.0 | ..... | ..... | ..... | ..... |
| 47 | 29 | ..... | 450.76 | 3716. | 3715.5 | +0.5 | +0.1 | ..... | ..... | ..... | ..... |
| 48 | 29 | ..... | 1057.32 | 10190.5 | 10186.7 | +3.8 | +0.3 | ..... | ..... | ..... | ..... |
| 49 | 29 | ..... | 1057.09 | 10188. | 10184.1 | +3.9 | +0.3 | ..... | ..... | ..... | ..... |
| | 29 | 287.55 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| | May 1–10 | ..... | ..... | ..... | ..... | ..... | ..... | F 3400 | 9046. | ..... | ..... |
| | | | | | | | | M3400 | 9050 | | |
| 50 | 13 | ..... | 421.19 | 3430. | 3431.1 | −1.1 | −0.1 | ..... | ..... | ..... | ..... |
| 51 | 13 | ..... | 422.06 | 3438.5 | 3439.4 | −0.9 | −0.1 | ..... | ..... | ..... | ..... |
| 52 | 13 | ..... | 751.52 | 6771.5 | 6772.1 | −0.6 | −0.1 | ..... | ..... | ..... | ..... |
| 53 | 13 | ..... | 751.36 | 6769.5 | 6770.4 | −0.9 | −0.1 | ..... | ..... | ..... | ..... |
| 54 | 14 | ..... | 663.62 | 5845.5 | 5847.8 | −2.3 | −0.2 | ..... | ..... | ..... | ..... |
| 55 | 14 | ..... | 663.33 | 5848. | 5844.8 | +3.2 | +0.3 | ..... | ..... | ..... | ..... |
| 56 | 14 | ..... | 978.10 | 9274. | 9272.5 | +1.5 | +0.1 | ..... | ..... | ..... | ..... |
| 57 | 14 | ..... | 978.82 | 9281. | 9280.7 | +0.3 | 0.0 | ..... | ..... | ..... | ..... |
| 58 | 16 | ..... | 571.49 | 4907. | 4906.5 | +0.5 | +0.1 | ..... | ..... | ..... | ..... |
| 59 | 16 | ..... | 571.37 | 4906. | 4905.3 | +0.7 | +0.1 | ..... | ..... | ..... | ..... |
| 60 | 16 | ..... | 795.42 | 7242. | 7243.3 | −1.3 | −0.1 | ..... | ..... | ..... | ..... |
| 61 | 16 | ..... | 795.46 | 7243. | 7243.7 | −0.7 | −0.1 | ..... | ..... | ..... | ..... |
| 62 | 16 | ..... | 795.24 | 7240. | 7241.4 | −1.4 | −0.1 | ..... | ..... | ..... | ..... |
| 63 | 16 | ..... | 1056.91 | 10188. | 10182.0 | +6.0 | +0.5 | ..... | ..... | ..... | ..... |
| 64 | 16 | ..... | 1056.15 | 10177. | 10173.1 | +3.9 | +0.3 | ..... | ..... | ..... | ..... |
| 65 | 17 | ..... | 710.27 | 6338. | 6335.2 | +2.8 | +0.3 | ..... | ..... | ..... | ..... |
| 66 | 17 | ..... | 710.70 | 6341. | 6339.7 | +1.3 | +0.1 | ..... | ..... | ..... | ..... |
| 67 | 17 | ..... | 888.96 | 8272. | 8268.5 | +3.5 | +0.3 | ..... | ..... | ..... | ..... |
| 68 | 17 | ..... | 889.50 | 8277. | 8274.5 | +2.5 | +0.2 | ..... | ..... | ..... | ..... |
| 69 | 17 | ..... | 955.74 | 9024. | 9018.2 | +5.8 | +0.5 | ..... | ..... | ..... | ..... |
| 70 | 17 | ..... | 955.01 | 9015. | 9009.9 | +5.1 | +0.5 | ..... | ..... | ..... | ..... |
| 71 | 18 | ..... | 468.56 | 3891. | 3888.0 | +3.0 | +0.3 | ..... | ..... | ..... | ..... |
| 72 | 18 | ..... | 468.94 | 3894.5 | 3891.7 | +2.8 | +0.3 | ..... | ..... | ..... | ..... |
| 73 | 18 | ..... | 839.95 | 7730. | 7727.8 | +2.2 | +0.2 | ..... | ..... | ..... | ..... |
| 74 | 18 | ..... | 839.46 | 7725. | 7722.4 | +2.6 | +0.2 | ..... | ..... | ..... | ..... |
| 75 | 18 | ..... | 930.70 | 8741. | 8735.4 | +5.6 | +0.5 | ..... | ..... | ..... | ..... |
| 76 | 18 | ..... | 930.62 | 8740. | 8734.5 | +5.5 | +0.5 | ..... | ..... | ..... | ..... |
| | 19 | 287.63 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| | 20–22 | ..... | ..... | ..... | ..... | ..... | ..... | F 3398 | 9040 | 10212 | ..... |
| | | | | | | | | M3398 | 9040 | 10216 | |
| | 23 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | F 9042 | ..... | ..... |
| | | | | | | | | | M9042 | | |

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TABLE IV.

$e = -305.5 + 8.1749\, t + 0.001654\, t^2$.

| Number of observation. | Observed temperature, gas thermometer. | Observed electromotive force, element *W*. | Calculated electromotive force. | Obs.− Calc. | Obs.− Calc. |
|---|---|---|---|---|---|
| | ° | *mv.* | *mv.* | *mv.* | ° |
| 1, 2, 5, 6, 13, 14, 26, 27, 50, 51. | 418.97 | 3407.7 | 3409.9 | −2.2 | −0.2 |
| 46, 47 | 450.88 | 3717.0 | 3716.6 | +0.4 | 0.0 |
| 71, 72 | 468.75 | 3892.8 | 3889.9 | +2.9 | +0.3 |
| 30, 31 | 489.84 | 4096.0 | 4095.7 | +0.3 | 0.0 |
| 28, 29 | 519.89 | 4390.5 | 4391.6 | −1.1 | −0.1 |
| 36, 37 | 550.73 | 4699.3 | 4698.3 | +1.0 | +0.1 |
| 58, 59 | 571.43 | 4906.5 | 4905.9 | +0.6 | +0.1 |
| 32, 33 | 587.99 | 5073.0 | 5073.0 | 0.0 | 0.0 |
| 42, 43 | 644.31 | 5647.0 | 5648.2 | −1.2 | −0.1 |
| 54, 55 | 663.48 | 5846.8 | 5846.4 | +0.4 | 0.0 |
| 34, 35 | 688.14 | 6101.8 | 6103.1 | −1.3 | −0.1 |
| 65, 66 | 710.49 | 6339.5 | 6337.5 | +2.0 | +0.2 |
| 52, 53 | 751.44 | 6770.5 | 6771.3 | −0.8 | −0.1 |
| 38, 39 | 769.18 | 6959.8 | 6960.9 | −1.1 | −0.1 |
| 60, 61, 62 | 795.37 | 7241.7 | 7242.8 | −1.1 | −0.1 |
| 73, 74 | 839.71 | 7727.5 | 7725.1 | +2.4 | +0.2 |
| 40, 41 | 867.22 | 8024.8 | 8027.7 | −2.9 | −0.3 |
| 67, 68 | 889.23 | 8274.5 | 8271.6 | +2.9 | +0.3 |
| 75, 76 | 930.66 | 8740.5 | 8734.9 | +5.6 | +0.5 |
| 44, 45, 69, 70 | 956.68 | 9032.2 | 9028.9 | +3.3 | +0.3 |
| 56, 57 | 978.46 | 9277.5 | 9276.6 | +0.9 | +0.1 |
| 19, 20 | 1012.80 | 9667.5 | 9670.4 | −2.9 | −0.3 |
| 24, 25 | 1032.73 | 9895.3 | 9900.8 | −5.5 | −0.5 |
| 48, 49, 63, 64 | 1056.87 | 10185.9 | 10181.5 | +4.4 | +0.4 |
| 17, 18, 21, 22, 23 | 1078.31 | 10430.0 | 10432.5 | −2.5 | −0.2 |

In their paper on the electromotive force of metals of the platinum group, Holborn and Day[1] have shown that the relation between the thermo-electric force and the temperature could be represented, within wide limits, with an accuracy of ± 1.0° by a function of the second degree. The results of our measurements are represented by a function of the second degree, between 400° and 1100°, with an average error somewhat less than 0.2°, the maximum error reaching 0.5° in two cases.

After the series of observations represented by Tables III and IV, the bulb was evacuated and refilled with nitrogen under a somewhat higher initial pressure, $p_0 = 325$ mm. With this filling, the results contained in Table V were obtained. Column 5 of this table contains the differences between the observed electromotive forces and the electromotive forces calculated with the equation:

$$e = -265.6 + 8.0784\, t + 0.0017124 t^2.$$

The average difference is 0.16°, the maximum difference 0.5°.

[1] Am. Journ. Sci. (4), 8, 303–308, 1899.

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TABLE V.

Thermo-couple *W*. Initial pressure 325 mm. $\alpha = 0.003665$.
Equations used for calculated temperatures:

$$e = -265.6 + 8.0784t + 0.0017124t^2$$
and $e = -305.5 + 8.1749t + 0.001654t^2$ (last column parentheses).

| Date. | Observed temperature, gas thermometer. | Observed electromotive force, element *W*. | Calculated electromotive force | Obs.−Calc. | Obs.−Calc. |
|---|---|---|---|---|---|
| 1907. | ° | *mv.* | *mv.* | *mv.* | ° |
| June 3... | 482.10 | 4025. | 4027.0 | −2.0 | (+0.5)−0.2 |
| | 482.15 | 4026. | 4027.5 | −1.5 | (+0.6)−0.1 |
| | 581.29 | 5009. | 5008.9 | +0.1 | (+0.4) 0.0 |
| | 582.22 | 5017.5 | 5018.2 | −0.7 | (+0.3)−0.1 |
| | 675.07 | 5974. | 5968.3 | +5.7 | (+0.7)+0.5 |
| June 4... | 700.88 | 6238.5 | 6237.6 | +0.9 | (+0.2)+0.1 |
| | 701.05 | 6239. | 6239.4 | −0.4 | (+0.1) 0.0 |
| June 6... | 772.10 | 6992. | 6992.6 | −0.6 | ( 0.0)−0.1 |
| | 771.72 | 6988. | 6988.5 | −0.5 | ( 0.0) 0.0 |
| May 29.. | 819.00 | 7495. | 7499.2 | −4.2 | (−0.4)−0.4 |
| June 4... | 860.52 | 7954. | 7954.0 | 0.0 | (−0.2) 0.0 |
| | 860.47 | 7952. | 7953.5 | −1.5 | (−0.1)−0.1 |
| June 5... | 908.47 | 8488.5 | 8486.7 | +1.8 | (+0.2)+0.2 |
| | 908.57 | 8488.5 | 8487.8 | +0.7 | (+0.1)+0.1 |
| June 4... | 955.30 | 9016. | 9014.4 | +1.6 | (+0.3)+0.1 |
| | 954.91 | 9011. | 9010.0 | +1.0 | (+0.2)+0.1 |
| June 5... | 995.32 | 9474. | 9471.4 | +2.6 | (+0.5)+0.2 |
| | 995.86 | 9480. | 9477.6 | +2.4 | (+0.4)+0.2 |
| June 6... | 1038.82 | 9975. | 9974.3 | +0.7 | (+0.3)+0.1 |
| | 1035.65 | 9940. | 9937.5 | +2.5 | (+0.5)+0.2 |
| | 1058.50 | 10197.5 | 10204.0 | −6.5 | (−0.3)−0.5 |

The agreement between this series of observations (Table V) and the preceding one (Tables III and IV) is also remarkably close. Perhaps this is best shown by the fact that the same equation used for the "calculated" values in Tables III and IV will represent the observations of Table V also with ample accuracy for purposes of interpretation. These differences are carried out in parentheses in the last column as an added evidence of the general agreement of all the experimental results. It will be remembered that the initial gas pressure and therefore the sensitiveness of the instrument, together with all the correction factors which depend upon it, were changed for the observations of Table V.

## MELTING-POINTS BASED ON FIRST SERIES (PT-IR BULB).

Four metal melting-points were used to fix the gas-thermometer temperatures of the preceding tables—zinc, silver, gold, and copper. Analyses of the metals are given on page 85. The melting-point determinations (except gold, of which the only sample then available accidentally became contaminated with iron during the observations and could no longer be used as a standard) are contained in Table VI.

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TABLE VI.—TEMPERATURE OF FIXED POINTS.

FIRST SERIES, PLATIN-IRIDIUM BULB.

ZINC.

| Number (from Table III). | Date. | Element *W* in gas-thermometer furnace. | Gas-thermometer temperature. | Element *W* in zinc bath. | Observed temperature of melting zinc. |
|---|---|---|---|---|---|
| | 1907. | *mv.* | ° | *mv.* | ° |
| 1 | Mar. 6 | 3367. | 414.49 | 3405. | 418.5 |
| 2 | Mar. 6 | 3371. | 414.96 | 3405. | 418.5 |
| 5 | Mar. 7 | 3416. | 419.96 | 3405. | 418.8 |
| 6 | Mar. 7 | 3417. | 420.00 | 3405. | 418.7 |
| 13 | Mar. 12 | 3430. | 421.50 | 3405. | 418.9 |
| 14 | Mar. 12 | 3429. | 421.50 | 3405. | 419.0 |
| 26 | Apr. 23 | 3383. | 416.14 | 3405. | 418.4 |
| 27 | Apr. 23 | 3384. | 416.26 | 3405. | 418.4 |
| 50 | May 13 | 3430. | 421.19 | 3400. | 418.0 |
| 51 | May 13 | 3439. | 422.06 | 3400. | 418.0 |

Melting-point of zinc (Pt-Ir bulb)—Mean..... 418.5°
Average error..... 0.3°

SILVER.

| | | | | | |
|---|---|---|---|---|---|
| 44 | Apr. 27 | 9036. | 957.20 | 9045. | 958.0 |
| 45 | Apr. 27 | 9054. | 958.81 | 9045. | 958.1 |
| 56 | May 14 | 9274. | 978.10 | 9045. | 958.1 |
| 57 | May 14 | 9281. | 978.82 | 9045. | 958.2 |
| 69 | May 17 | 9024. | 955.74 | 9042. | 957.3 |
| 70 | May 17 | 9015. | 955.01 | 9042. | 957.4 |
| — | June 4 | 9016. | 955.30 | 9042. | 957.6 |
| — | June 4 | 9011. | 954.91 | 9042. | 957.6 |

Mean..... 957.8°
Average error..... 0.3°
Approximate correction for loss of heat at ends of bulb. +2.°

Melting point of silver (Pt-Ir bulb)..... 960°

COPPER.

| | | | | | |
|---|---|---|---|---|---|
| 17 | Mar. 15 | 10430.5 | 1078.02 | 10461. | 1080.5 |
| 18 | Mar. 15 | 10419. | 1077.05 | 10461. | 1080.5 |
| 21 | Mar. 20 | 10446. | 1079.96 | 10456. | 1080.9 |
| 22 | Mar. 20 | 10426. | 1078.26 | 10456. | 1080.8 |
| 23 | Mar. 20 | 10434. | 1079.02 | 10456. | 1080.9 |

Mean..... 1080.7°
Average error..... 0.2°
Approximate correction for loss of heat at ends of bulb. +2.°

Melting-point of copper (Pt-Ir bulb)..... 1083°

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This work with the platin-iridium bulb developed two serious limitations which have received detailed consideration and correction elsewhere (pp. 50 and 51). They are these:

(1) Independent end coils wound on the furnace tube (see Fig. 1) can be made to give perfectly uniform temperature distribution along the sides of the bulb from end to end, but not on the end surfaces.

(2) The sublimation of the iridium in the bulb, while not prohibitive below 1100°, affects the homogeneity of thermo-elements during the exposure necessary to calibrate them, at temperatures above 900°, to an extent which greatly limits their subsequent usefulness.

This second limitation led to the substitution of a bulb containing rhodium in place of iridium, but does not seriously affect the results already obtained with the platin-iridium bulb, which were all below 1100° (Tables III, IV, V). The first limitation, on the other hand (the cooling of the end surfaces of the bulb by radiation), was not detected until the observations with the platin-iridium bulb were completed and published and the bulb itself was returned to the maker. It is therefore no longer possible to supply a correction factor made with the same bulb under identically the same conditions with which to compensate the error in the final temperatures of Table VI. The new platin-rhodium bulb, however, except for the reentrant tube below, was of the same dimensions as the old one and the furnace conditions were very closely reproducible. A measurement was accordingly made with the new bulb as nearly as possible under the conditions previously employed and another with a diafram in the tube to cut off and reflect back the radiation going out from the upper end of the bulb. The temperature was that of melting copper (1082.6°). This diafram above the bulb raised the gas thermometer temperature 0.9°. A similar test for the effect of radiation from the bottom could not be made, but it was probably of similar magnitude. The total error incurred in the above measurements through the radiation from the ends of the bulb would therefore be of the order of magnitude 2° at the copper-point. At low temperatures the effect is too small to make it worth while estimating a correction factor. If we then suppose the radiating power of the 20 per cent platin-rhodium alloy to be comparable with that of the iridium alloy, one may apply this correction to the mean temperatures obtained with the platin-iridium bulb as given in Table VI. While these values are in good agreement with the later results obtained with the platin-rhodium bulb, they are not included in Table XIX because of the approximative character of this ex-post-facto correction.

## 10. INTRODUCTION TO THE SECOND SERIES, INCLUDING THE HIGHER TEMPERATURES, 1100°–1600°.

Above 1100° considerable uncertainty has existed in the temperatures of various fixed points. The melting-point of nickel, determined by extrapolation from the data of Holborn and Wien (1484°),[1] has been frequently employed. The curve of the platinum-platinrhodium thermo-element, extrapolated beyond the copper-point, has been still more generally used, but like most extrapolations, may lead to quite erroneous results. The only gas-thermometer comparison that has been made in this region is that

[1] Holborn and Wien, Wied. Ann. 47, 107–134, 1892; and 56, 360–396, 1895.

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of Holborn and Valentiner,[1] but by their own estimate the accuracy of the upper portion of their scale is not greater than ±10°. The chief purpose of our work was, therefore, to establish the temperature of several fixed points between 1100° and 1600° and to ascertain what curve is followed by the platinum-platinrhodium thermo-element in this region, with an accuracy comparable to that obtained in the lower portion.

The plan of procedure is simple. It consists, first, in selecting certain fixed thermometric points, usually melting-points of metals, and in determining their reproducibility; second, in making a measurement of the true temperature on the nitrogen scale at or close by these fixed points; third, in transferring these known temperatures by means of a thermo-element over to the fixed points selected. This transference by the thermo-element is necessary because the thermometer bulb can not be put directly into melting or solidifying substances at high temperatures. The relation of electromotive force to temperature for any particular kind of thermo-element does not enter into the problem when the temperatures measured are close to the fixed points; a linear correction is then abundantly accurate. The interpolation curve, for any element, between the fixed points established by the gas thermometer is therefore a separate matter.

No other method of transferring the gas-thermometer temperatures can be employed in this region. Of the two methods of comparative temperature measurement in common use, one, the platinum resistance pyrometer, can not be used above 1100° with certainty—the other, the radiation pyrometer, is of wholly inadequate sensitiveness in any of the forms hitherto devised.

The questions which remain to be answered are, then: (1) How exact and uniform can the temperature of the gas in the bulb be made (independently of any effort to measure this temperature)? (2) How accurately can its pressure be measured in order to establish that temperature on the nitrogen scale? (3) How accurately can this temperature be transferred from the thermometer and compared with the fixed melting-point? (4) How accurately can the fixed points be reproduced for purposes of calibration of secondary measuring devices?

As has been stated, our experience has convinced us that most of the variations in the gas-thermometer temperatures of the fixed points commonly used by various observers, are due, not to differences in the properties of different gases, nor to differences in pressure, nor to differences between the constant-volume and constant-pressure scales, all of which have been frequently discussed from the theoretical standpoint; but to systematic errors residing in the apparatus and the methods employed. A large portion of the present work has therefore been devoted to finding out experimentally the effect of variations in all those conditions which might affect the results systematically.

[1] Ann. d. phys. (4), **22**, 1–48, 1907.

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## 11. CHANGES IN THE APPARATUS.

In all essentials the gas-thermometer apparatus used for this second series of measurements is identical with that already described, except for the bulb.

### THE PLATIN-RHODIUM BULB.

Primarily and obviously, the bulb must be able to hold the expanding gas without absorbing or losing any portion of it throughout the temperature range of the measurements. A secondary requirement, the importance of which increases rapidly when high accuracy is sought, is that it shall be possible to use several thermo-elements in the furnace with the bulb without their readings being endangered by contamination from the bulb material. As long as this intermediary role of the thermo-element remains a necessary one and alloys of platinum continue to provide the only successful bulb material, the contamination[1] of the platinum wire of the element by the alloyed iridium or other platinum metal in the bulb will remain a serious consideration in all temperature measurement above 900°.

Although the platin-iridium bulb served well as a gas-container, the contaminating effect of the iridium upon the thermo-elements made the life of the latter, for measurements of this degree of accuracy, very short. Accordingly, at the close of the first series of experiments, a change was made from the platin-iridium bulb to one of platin-rhodium (80 parts platinum, 20 parts rhodium) 160 mm. long and 47 mm. in diameter. Inasmuch as one of the wires of the thermo-element itself contains 10 per cent of rhodium to which the platinum wire is always exposed (and which gradually contaminates it, too, although very slowly[2]), it was thought that the substitution of a rhodium alloy in the bulb might serve to retain the necessary qualities of stiffness and regularity of expansion with a minimum of disadvantage in the matter of contamination. These expectations have been completely realized. Although the rhodium alloy is less rigid at temperatures of 1000° and beyond than the iridium alloy, and requires more careful adjustment for equal pressure within and without, no sagging of the bulb walls or deformation from the gas pressure has appeared up to 1550°. Meanwhile, the contamination of the thermo-elements in the presence of the rhodium alloy is now reduced to about 20 per cent of its former magnitude for a given temperature and time of exposure.

### THE FURNACE.

The common practice of recent observers (Callendar, Harker, Holborn and Day, Jaquerod and Perrot) has been to use a cylindrical bulb in which the length was three or four times the diameter, inclosed in a concentric furnace tube (air-bath) heated by the electrical resistance of a coil of wire wound upon or within it. To this bulb the heat is applied radially over its cylindrical surface, but no heat is supplied at the ends. The furnace tube itself and the winding of the coils have been changed at different times and in a variety of ways in order to vary the distribution of the heat supply. The arrangement which has become usual with us is to wind the coil somewhat more closely at the ends than the middle, with the idea of providing

[1] For a detailed account of the behavior and treatment of contaminated thermo-elements, see Walter P. White, Phys. Rev., **23**, 449–474, 1906.

[2] White, "Constancy of thermo-elements." Phys. Rev., **23**, 463–465, 1906. Phys. Zeitschr., **8**, 331–333, 1907.

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partial compensation for the inevitable heat losses at the ends of the furnace in this way, and, in addition, to insert supplementary coils of smaller wire in the ends of the furnace tube in order to provide a small, independently regulated heat supply which can be superposed upon that of the main coil and give the desired uniformity at any temperature likely to be employed. A furnace tube arranged in this way, except for accidental variations, caused, for example, by the flaking off of the furnace lining, affords uniform temperature distribution over a length of 20 cm. in the center of the tube for a range of temperature from 300° to 1550°, and no one temperature is more difficult to regulate than another. This arrangement contains a limitation, however, of considerably greater magnitude than was at first suspected. The ends of the bulb face the comparatively cold ends of the furnace tube and radiate a sufficient quantity of heat toward these cold ends to reduce the temperature of the end surfaces of the bulb some 6° or 8° below the mean temperature of the cylindrical surface.

This may appear to be a rather obvious condition to be overlooked, but it is a common practice of physicists to assume that the temperature is constant over a radial cross-section near the center of a cylindrical furnace which is reasonably long in comparison with its diameter. With this in mind, the probability is even greater that a metallic conductor only 4 cm. in diameter (the end surface of the bulb), perpendicular to the axis in such a furnace, will have a uniform temperature between its center and periphery. The fact is that neither of these assumptions is justified, even in furnaces as long as twenty times the diameter. This was shown in a number of actual measurements made in different furnaces under varied conditions, differences of several tenths of a degree being found as low as 300°, and of several degrees at 1000° and higher.

This situation demonstrates the futility of depending upon metallic conductivity (of platinum) to equalize a steep temperature gradient, and again emphasizes the fact that the air-bath, or, more explicitly, the temperature distribution within the heating chamber, is the most uncertain factor remaining in gas thermometry.

On account of difficulties in manipulation and accidental leakage into the thermo-element system, we preferred not to introduce more heating coils into the furnace tube and therefore undertook to stop the loss of heat by inserting thin, platinum-covered diaframs opposite the ends of the bulb. The situation was still further safeguarded, in exchanging the platin-iridium for the platin-rhodium bulb, by adding a reentrant tube at the lower end of the bulb, to enable us to measure the actual temperature prevailing at its center as well as over the surface. We thought thus to obtain a more representative integral of the surface temperature and a competent comparison of this integral with the temperature actually prevailing at the center of the bulb.

Only one change was made in the manometric apparatus. The gas, instead of being introduced through the three-way cock at the bottom of the short arm of the manometer, which necessitated its bubbling through the mercury, was admitted by a stopcock and a slanting side tube blown into the manometer tube about 30 cm. below the fixed point.

Changes in the expansion-coefficient apparatus are described on p. 61.

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## 12. DETAILS, ERRORS, AND CORRECTIONS.

The gas thermometer for very high temperatures has now reached a stage of development where it becomes necessary to examine many small sources of error. These will be discussed in the succeeding paragraphs without attempting to classify separately the variable errors of observation, and the systematic errors which may arise from conditions of the measurements or from constant corrections.

To bring out the plan of investigation of these errors, it will be well to recall the derivation of the gas-thermometer formula. The gas scale, as is well known, is defined by the relation

$$\frac{pv}{1+at}=K \tag{1}$$

in which $K$ and $a$ are constants and $t$ is a function of the product $pv$, $p$ and $v$ being the pressure and volume of a fixed mass of the gas. $K$ and $a$ are determined by two further conventions:

When $p=p_0$ and $v=v_0$ (at the melting-point of ice), $t=0$ (2)

When $p=p_{100}$ and $v=v_{100}$ (at the boiling-point of water), $t=100$ (3)

It is then evident that

$$a=\frac{p_{100}\frac{v_{100}}{v_0}-p_0}{100p_0}$$

which defines $a$ as the mean pressure-coefficient of the gas between 0° and 100° (when $v_{100}$ and $v_0$ are nearly equal); and

$$K=p_0v_0$$

The temperature $t$ is therefore defined by the formula

$$t=\frac{p\frac{v}{v_0}-p_0}{ap_0} \tag{4}$$

the scale depending upon the gas chosen, the value of $p_0$, and the ratio $\frac{v}{v_0}$. In the theoretical constant-volume thermometer this ratio $\frac{v}{v_0}$ is unity, but in the experimental constant-volume thermometer it always varies considerably from 1. We have therefore preferred to treat equation (4) as the fundamental equation, introducing in place of $\frac{v}{v_0}$, however, the proper function of the expansion coefficient of the bulb material.

Since apparatus designed for high-temperature work is not suited for the most accurate determination of $a$, $a$ has been treated in this discussion as a separately determined constant.

In the experimental gas thermometer there is always a small space in the tube connecting with the manometer, and this space is at various temperatures other than $t$. The pressure ($p'$ or $p_0'$) actually measured is not,

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therefore, the $p$ or $p_o$ of the formula. Imagine that this supplementary space is heated up to the uniform temperature $t$, without any change in its volume, and let the resulting corrected pressure be $p$ (or $p_o$ as the case may be). Furthermore, let

$V$ = volume of bulb at $t°$.
$V_o$ = volume of bulb at o°.
$v_1$ = volume of unheated space, which is at temperatures other than $t$ (or than o°).
$t_1$ = temperature of this space.
$\beta$ = linear expansion coefficient of the bulb material.

Under these conditions, formula (4) becomes:

$$t = \frac{1}{p_o a}\left[p\frac{V+v_1}{V_o+v_1} - p_o\right]$$

Since

$$\frac{V+v_1}{V_o+v_1} = \frac{\frac{V}{V_o}+\frac{v_1}{V_o}}{1+\frac{v_1}{V_o}} = \frac{1+3\beta t+\frac{v_1}{V_o}}{1+\frac{v_1}{V_o}} = 1+\frac{3\beta t}{1+\frac{v_1}{V_o}}$$

the formula for $t$ becomes

$$t = \frac{1}{p_o a}\left[p\left(1+\frac{3\beta t}{1+\frac{v_1}{V_o}}\right) - p_o\right] \qquad (5)$$

In this formula $\frac{v_1}{V_o}$ is a very small correction term; while the important quantities to be measured are $p_o$, $p$, $a$, and $\beta$. The ratio $\frac{v_1}{V_o}$ becomes of importance, however, in determining the corrected pressure $p$ from the measured pressure $p'$. The derivation of this correction is as follows:

The mass of the gas in the unheated volume under the actual conditions of measurement is proportional to $\frac{p'v}{1+at_1}$; the mass of the gas within the bulb is proportional to $\frac{p'V}{1+at}$. If we now suppose the unheated space raised to the uniform temperature $t$ without change of volume, the pressure being thereby raised to $p$, the total mass is proportional to $\frac{p(V+v_1)}{1+at}$. Therefore,

$$\frac{p'v_1}{1+at_1} + \frac{p'V}{1+at} = \frac{p(V+v_1)}{1+at}$$

whence

$$p-p' = p'\left(\frac{v_1}{V+v_1}\cdot\frac{at-at_1}{1+at_1}\right)$$

This correction is easily calculated and tabulated; or, better, the factor in parenthesis (in the second member of the equation) is plotted against temperature. In practice, the volume $v_1$ is divided into three portions at temperatures $t_1'$, $t_1''$, and $t_1'''$ as explained on page 58, and the correc-

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tions obtained from the curve for each of these portions are simply added together to obtain the total correction $p-p'$. With these corrected pressures, $p_0$ and $p$, the temperature $t$ is calculated by formula (5) on page 53.

This method of computation yields, of course, the same values for $t$ as the formula on page 40, but has the advantage of showing more clearly the magnitude of the corrections.

The discussion of errors and corrections will now be taken up under the general outline sketched on page 49.

## TEMPERATURE OF THE GAS IN THE BULB.

*Uniformity.*—Above the temperatures where a liquid or vapor bath can be used to secure uniformity, the differences of temperature between different parts of a furnace have always been a serious limitation to the accuracy of the gas thermometer. This variation, even in a furnace containing well-conducting materials, is much larger than has usually been assumed, and the three equalizing factors of conductivity, radiation, and convection by air-currents are all credited with much greater influence in bringing about uniformity than they really possess. It sometimes happens that our faith in these factors is inversely proportional to our quantitative information about them.

In the first measurements with the new bulb, the end elements were placed on the axis of the bulb, in positions 1 and 9 (Fig. 8), instead of on the periphery of the cylinder. It became evident at once that the supporting tube in the bottom of the furnace, used in earlier measurements, had a considerable cooling influence on the central portion of the bottom, an effect which would tend to make the results low. This effect was largely obviated by replacing the heavy magnesite tube (Fig. 1, p. 18) with a thin Marquardt porcelain tube, in the top of which was placed a Marquardt crucible, cut out into a three-pronged support (Fig. 9, p. 56). The bottom of the crucible acted as a screen to prevent radiation from the bottom of the bulb, and the smaller thickness and thermal conductivity of the tube practically prevented the loss of heat from the bottom by conduction. Later, a second diafram was added about 1 cm. lower down, primarily for the purpose of centering the tube and bulb in the furnace, but without noticeable effect on the temperature distribution.

In addition to the three thermo-elements mentioned, a fourth was located inside the reentrant, in position 8.[1] Several trials under varied conditions confirmed the fact that this element, when the other three were set equal, was 2° to 3° hotter than the one on the outside. A thorough exploration of the distribution of temperature over the surface of the bulb was therefore undertaken.

Since the number of wires which could be led out through the packed joints was limited, the plan was adopted of using the bulb itself as a differential thermo-element, single platinum wires being tied to the bulb at points whose temperature was to be determined. Each of these wires formed, with the platinum of the standard element tied to the bulb at the middle, a differential element which would read zero if the wires were alike and if no difference of temperature existed between the two points on the bulb.

[1] See Fig. 8, and note, p. 55.

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The relation of the wires was established by sealing each in turn to the platinum of the standard, and measuring their E. M. F. at various temperatures. The readings varied, according to the quality of the wire, from 0 to 40 microvolts. The method of evaluating differences of temperature, when such existed, is discussed on page 66.

The distribution of temperature lengthwise of the bulb was first investigated, and auxiliary wires were placed at the levels 1 (base of stem), 2 (top shoulder), 6 (bottom shoulder), 7 (bottom, outside of funnel), in addition to thermo-elements at 4 (middle outside), 8 (inside reentrant), and 9 (bottom, just inside of funnel).[1]

With this system of thermo-elements, it was found that at 1082°, when 9 was brought to equality with 4 and 1, then at the bottom of the bulb element 6 was superheated 6° to 8° and element 7 about 4°, due entirely to the fact that the thermo-element at 9, not being in contact with the bulb, lost sufficient heat by conduction and radiation downward to keep its temperature below that of the metal surrounding it. The element 8, on the other hand, received heat by conduction up the reentrant tube and by radiation from below, which made it read higher than the element at the same level outside. The element at position 9 was therefore discarded and each setting of temperature was made with the elements which were attached directly to the bulb, *i. e.*, by bringing 1, 4, and 7, or 2, 4, and 6 to uniform temperature. In fact, at the highest temperatures where the danger of unequal distribution was greatest, both arrangements were employed in successive measurements at each temperature.

The temperature between the middle and the top shoulder was also examined in several experiments. The temperature at this position was found to be within 0.5° of the other two, with a tendency to be lower than these.

Further experiments showed that, in addition to the possibility of vertical variation of temperature, there was a variation around the circumference of the bulb. This amounted in the worst case (at 1450°) to a variation of 1.3° from the mean, four elements being used around the circumference to make the test. This variation seemed to be due either to unequal conductivity of the furnace material at different points or to the flaking off of small portions of the furnace lining, leaving exposed places on the wire. Variations of this character are probably an unavoidable result of using a furnace where the heat supply is so near to the point where it is measured, as is the case with the furnace coil which is wound on the inside of the tube. This form of winding is necessary, however, in order to reach the highest temperatures, so that absolute uniformity of temperature around the bulb was sacrificed to the increased range of the instrument.

After this variation was discovered, measurements were always made with four elements at equal distances around the circumference of the bulb and the mean of their readings was taken.

In order to be perfectly certain that no systematic error was being introduced by using this one form of furnace (Fig. 9) throughout, it was replaced

[1] The system of numbering the positions of elements on the bulb is shown in Fig. 8. The figure before the decimal point indicates the horizontal level, the figure after the decimal indicates the orientation around the bulb. For instance, an element in position 3.5 would be about half-way between the top and middle and on the side of the bulb away from the front of the apparatus.

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temporarily by a furnace of platinum wire wound on the *outside* of a similar tube. In this way a heavy mass of good heat-conducting material was introduced between the source of heat and the bulb, with the expectation that a more uniform temperature might thereby be obtained in the inside space. The two types of furnace are shown in Figs. 9 and 10.

A measurement at the copper point with the outside-wound furnace gave as the melting-point of copper 1082.6°, a value identical with the mean of the results obtained with the other furnace, thus proving that no systematic error need be feared from the inside-wound type of furnace. The horizontal uniformity obtained in the outside-wound furnace was better than that in

FIG. 9. FIG. 10.

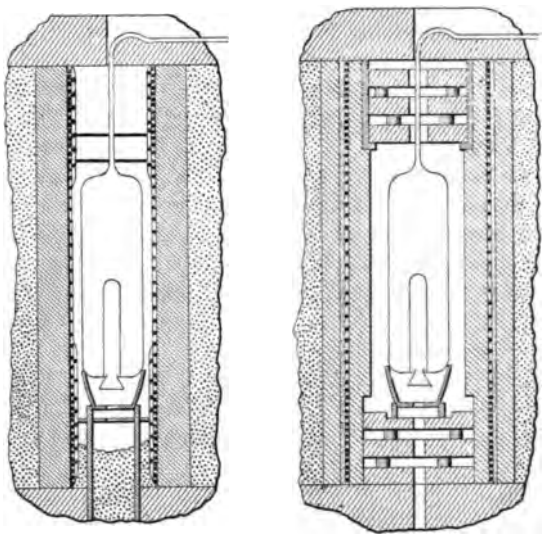

FIG. 9. Section of furnace and bulb showing an arrangement of coils and diaframs about the bulb which gave a most uniform temperature distribution in the measurement of both high and low temperatures. The supplementary end coils were independently heated and regulated.

FIG. 10. A special arrangement of the heating coil and diaframs designed to give a very uniform temperature distribution about the bulb. The coil was heavily ballasted inward with a good heat conductor and outward with a poor conductor. The heating coil was also divided into three sections which could be independently regulated. This furnace was used at the copper point only.

the inside-wound, but the furnace was more difficult to regulate and to hold at a given temperature.

*Constancy of conditions.*—Several causes interfered with the establishment of a constant temperature for observation. The three heating currents required constant observation and readjustment with the gradual extension of the heated zone toward the outside of the furnace. This came to equilibrium for a particular temperature after about half an hour, after which the bulb was held steady 15 to 30 minutes longer before readings of the pressure were taken. The temperature thus established could be relied upon to remain constant to within 1 to 3 microvolts (0.1° to 0.3°) during the course of the pressure measurements.

Above 1100° a noticeable leakage of current from the heating coil into the bulb and thermo-elements frequently appeared. This may have been

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due in part to conductivity across the narrow air-space between bulb and coil, but was probably chiefly due to accidental contact between the protecting tube of one of the thermo-elements and the furnace wall. To obviate any uncertainty from this cause, it was found necessary to use alternating current for all temperatures above 1100°. This was less easy to regulate than the direct current from storage batteries, but by careful regulation of the voltage of the motor generator supplying the alternating current, equally satisfactory results were obtained.

The constancy and exactness of the temperature at 0° were beyond question. On several occasions pressure measurements at 0° were made at intervals of 30 to 60 minutes and no measurable difference was found. Similarly, repacking the bulb in a fresh supply of ice gave exactly the same value.

## DEFINITION OF TEMPERATURE BY MEASUREMENT OF PRESSURE.

The procedure in measuring the pressure, $p'$, was as follows: First the three mercury thermometers on the manometer were read to determine the temperature of the mercury column and scale; then three to four settings of the barometer were made, alternating with measurements of the manometer. The mercury thermometers were read again at the close. During this interval the other observer made as many readings as possible of all the thermo-elements.

Before the manometer was connected to the bulb, the point on the scale corresponding to the reference point of the manometer[1] was determined once for all before the manometer was connected to the bulb, by connecting the two arms and raising the mercury to the point, as in a regular pressure measurement. Subsequent manometer readings were subtracted from this fixed level, and the resulting difference corrected for the temperature and calibration corrections of the scale and then reduced to 0°. The barometer reading was similarly corrected. The algebraic sum of the two gave the pressure $p'$, in terms of a centimeter of mercury at 0° and at the latitude and elevation of the laboratory. Since the absolute value of the pressure does not enter into the gas-thermometer formula, corrections for altitude and latitude are superfluous.

*Errors and Corrections in $p'$.*—The level of the fixed reference-point of the manometer varies with the temperature of the room because of the difference in expansion of the brass scale on the one hand and of the glass tube of the manometer which carries the fixed point on the other. This correction can be calculated from the expansion coefficients of the materials and amounts to 0.04 mm. per 5°. Its direction and amount were checked experimentally by determining the fixed point at two temperatures differing by about 10°, the room being open on a cold day for the one case, and closed and heated for the other. The difference found was 0.09 mm., and that calculated 0.08 mm.

The lengths of the divisions of the brass scale were corrected for change of temperature by a formula determined for this scale at the Normal Aichungs-Kommission, the absolute length of the scale having been determined at 16°. In addition, calibration corrections, determined for each

[1] Pages 19 and 27.

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millimeter of the scale, were applied. The total scale correction was always less than 0.15 mm., hence the temperature measurement by the adjacent mercury thermometers was abundantly accurate for this purpose.

The length of the mercury column was reduced to 0° by the expansion coefficient given in the Landolt-Börnstein-Meyerhoffer Tabellen. This correction varied from 0 to about 3.00 mm. As the mercury thermometers were calibrated and read to 0.1° the uncertainty in this correction due to uncertainty in the room temperature may amount to 0.05 mm. For their calibration the mercury thermometers were compared with a Richter standard thermometer calibrated at the Reichsanstalt.

The barometer reading was corrected to 0° by the Landolt-Börnstein-Meyerhoffer table for barometer with brass scale. Two Fuess barometers were used. Both had been tested by the Bureau of Standards; one had an absolute correction of 0.06 mm., the other was exact. This was checked by direct comparison of the two. The variable error in the barometer is probably about the same as in the manometer reading (0.05 mm.). On a very windy day, or during the approach of a storm, the barometer was too unsteady to permit satisfactory measurements to be made.

A further small correction to the barometer was necessary to allow for the weight of the air column between the cup of the barometer and the top of the mercury in the open manometer column. This correction was appreciable, amounting to 0.16 mm. in the extreme case.

To give some idea of the effect of these small corrections upon the final temperature measurement, it may be added that 1.00 mm. corresponds approximately to 1°.

To determine the corrected pressure, $p$, from the measured pressure, $p'$, (see page 53), the volume of the unheated space, $v_1$, connecting the bulb with the manometer, must be known.[1]

TABLE VII.—UNHEATED SPACE.

| Space. | Volume before Apr., 1909. | Volume after Apr., 1909 | Uncertainty of volume. | Uncertainty of temperature. | Maximum effect, at copper point, of the errors. |
|---|---|---|---|---|---|
| | *cc.* | *cc.* | | ° | ° |
| Pt-Rh capillary, bulb to top furnace ($v_1'$) | 0.055 | 0.055 | 0.002 | 100 | 0.04 |
| Pt-Rh capillary, top to outside furnace ($v_1''$) | 0.086 | 0.086 | 0.003 | 50 | 0.20 |
| Pt-Rh capillary to gold capillary ($v_1'''$) | 0.102 | 0.054 | 0.015 | 0.5 | 0.20 |
| Gold capillary ($v_1'''$) | 0.094 | 0.066 | | | |
| Pt capillary and Ni valve ($v_1'''$) | 0.025 | 0.025 | | | |
| Space above meniscus ($v_1'''$) | 0.023 | 0.023 | | | |
| Total | 0.385 | 0.309 | | | 0.45 |

This was recalculated because the dimensions of the capillary of the second bulb were somewhat larger than those of the first. The figures are given in Table VII. This volume was reduced in April, 1909, by bringing the manometer closer to the furnace, since the water-jacket of the furnace cut off the heat so completely that there was no risk in bringing

[1] See discussion of this correction, p. 16.

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the manometer as close as possible (35 cm). The volume $v_1$ was thereby reduced from 0.39 cc. to 0.31 cc., and the ratio $\frac{v_1}{V_0}$ from 0.00187 to 0.00150.

The volume $V_0$, which enters into the correction term (see page 53) was determined by weighing the bulb empty, and filled with distilled water at a known temperature. A very accurate determination of this volume was not necessary, the important requirement being that the volume should not change during a run. A check on change of volume was obtained in the measurement of the value of $p_0$. The volume of the bulb at 0°, up to the base of the capillary stem, was found to be:

| | c.c. |
|---|---|
| On 13 June, 1908 (new) | 205.74 |
| On 18 June, 1908 (after 1450°) | 205.75 |
| On 20 April, 1909 | 205.82 |

The volume of the unheated space, $v_1$, was arbitrarily divided into three portions for the convenient determination of its average temperature, $t_1$. The first portion, $v_1$, extended from the base of the stem to the top of the upper brick of the furnace (see Fig. 1); the second portion, $v_1''$, included the capillary stem as far as the outside of the furnace; the third portion, $v_1'''$, extended to the surface of the mercury in the manometer and included all of that portion of the unheated space which remained at room temperature.

The temperatures of the portions $v_1'$ and $v_1''$ were determined by placing a thermo-element at different points along the stem during several of the runs. As this temperature does not need to be known accurately, a few measurements gave a sufficient indication of the distribution of temperature in the portion of the "unheated space" within the furnace.

A liberal estimate of the degree of uncertainty in the values of $v_1$ and $t_1$ has been made and is included in Table VII, together with the effect which such errors would have on the calculated temperature, $t$, at the copper point.

*Errors and Corrections in $p_0'$.*—The same instrumental corrections apply to $p_0'$ as to $p'$; but their proportional magnitude is, of course, larger. The values of the uncertainty in $t$ due to these small errors will be found in Table X, p. 69.

As appears in Table X, the largest possibility of error in $p_0$ comes from corrections for the temperature of the mercury columns. These errors always affect $p_0$ and $p$ in nearly equal magnitude and become negligible in their effect upon $p - p_0$, but appear (uncompensated) in $p_0$ in the denominator. See equation (5) p. 53. To insure the constancy and accuracy of the temperature of the mercury column, the manometer was jacketed over its entire length with a pasteboard jacket. This was sealed tight at the permanent joints, and built up in removable sections over the portion of the manometer through which the height of mercury varied. A current of air was circulated through this jacket by a large-capacity suction jet. At the same time an electric fan kept a rapid upward current of air flowing over the entire apparatus. The temperature of the room was also kept as nearly constant as possible. Under these conditions the measurement of $p_0'$ was reproducible within 0.02 to 0.03 mm., corresponding to about 0.2° at 1500°. This was checked experimentally on several occasions by

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making readings of $p_0'$ under different conditions of room temperature and barometric pressure.

Changes in the value of $p_0$ (the ice-point) after heating to high temperatures have always been disturbing factors in gas-thermometer measurements and have introduced uncertainties of a very intangible kind. This was especially true of the porcelain bulbs formerly used, where both changes of volume and emission or absorption of gases by the walls occurred. The restoration of the platinum metals to favor as materials for the gas-thermometer bulb has practically eliminated this uncertainty. During the present work small changes in the value of $p_0$ have frequently occurred after heating to a high temperature, which seem not to be due to any change in volume, for the determinations of the volume, $V_0$, given above (p. 59), show a total change after a year's work corresponding to less than 0.1 mm. in $p_0$. In the early part of the work, the passage through the bulb wall of hydrogen or some other gas produced by the reducing action of wood fiber in an asbestos board insulator within the furnace, was suspected as being the cause of irregularity, particularly in view of the fact that Holborn and Valentiner had difficulties from this cause.

Further, it was several times observed that heating the furnace and bulb to a higher temperature than they had reached before caused a slight increase in the value of $p_0$—whether due to some gas passing in from the outside or coming out of the wall of the bulb is not known. Air dried over calcium chloride was used outside of the bulb in the furnace inclosure throughout the work, and no indication was ever obtained of the passage of either oxygen or nitrogen through the wall of the bulb, since measurements at a given temperature (after the first heating to that temperature) gave the same value of $p_0$ within the error of measurement.

On one occasion an almost inappreciable leak in the manometer connection caused some uncertainty. All measurements affected by this error, when it was discovered, were rejected.

## THE GAS.

Since the gas-thermometer apparatus as arranged for high-temperature measurements is not suited to a determination of the value of $\alpha$ (the pressure coefficient of the gas from 0° to 100°) with an accuracy comparable to that attained by Chappuis,[1] the value of $\alpha$ was treated as a constant. The figures used were:

$$\text{For } p_0 = 345-347 \text{ mm.}, \quad \alpha = 3665.8\times10^{-6}$$
$$\text{For } p_0 = 217-221 \text{ mm.}, \quad \alpha = 3664.0\times10^{-6}$$

It will be recalled that a number of independent determinations of $\alpha$ for different pressures were made (p. 40) with the platin-iridium bulb, but they show no appreciable difference from those by Chappuis within the experimental error of the apparatus. The probable error in Chappuis's results is not great enough to affect the high-temperature values.

Pure nitrogen was used throughout as the thermometric gas.[2] The

[1] Trav. Mem. Bur. Int., 6 and 12, 1888 and 1902.

[2] It was prepared by dropping a solution of 200 grams of sodium nitrite dissolved in 250 grams of water into a warm solution containing 350 grams of ammonium sulphate and 200 of potassium chromate in 600 of water. It was passed through a mixture of potassium bichromate and sulphuric acid and stored over water. For use in the gas thermometer it was purified by passing through calcium chloride, hot copper gauze, potassium bichromate in sulphuric acid, 2 bottles potassium pyrogallate solution, sulphuric acid, calcium chloride, and phosphorus pentoxide.

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storage tank was refilled several times so that not all the gas was from the same original supply; the filling of the bulb was also changed several times. The bulb was first completely evacuated and heated to a high temperature, after which the connections and bulb were rinsed out several times with the purified gas before the final filling.

## EXPANSION COEFFICIENT OF THE BULB ($\beta$).

The substitution of a new alloy in place of the platin-iridium made necessary a new determination of the expansion coefficient of the bulb material. The method of its determination and the comparator used for the purpose have been fully described in the earlier pages of this paper (p. 27) and do not require to be repeated here.

Three additional precautions were taken in carrying out the measurements. The bar was increased in length to 500 mm. and in diameter to 6 mm., in order to increase the sensitiveness of the determination and the uniformity of temperature along the bar respectively. In this case the bar was also made at the same time and from the same alloy as the bulb itself, and was therefore identical with it in composition.[1]

In ruling the bar, the lines were spaced 0.2 mm. apart instead of 0.5 mm., as in the previous investigation. This enabled a greater number of observations to be made within a narrow region than before, and thus made it possible to avoid the error from parallax described on page 34.

The third precaution involved a slight change in the comparator itself, and was made at the suggestion of Chappuis. Our custom had been to verify the distance between the fixed hairs of the microscopes before and after each heating by measuring this distance in terms of a standard brass bar calibrated at the Bureau of Standards. The brass bar was then replaced by the platin-iridium bar before the heating began, and the length of the latter was measured in terms of the initial distance between the fixed hairs, at intervals of 50° or 100° up to 1000°. This mode of procedure involved the assumption that the agreement of the measurements made before and after heating afforded adequate proof that no change had taken place *during* heating. The justification for this assumption lay in the facts that—

(1) The furnace was completely water-jacketed to prevent any heat reaching the microscopes from the furnace.

(2) Suitable insulating material introduced between the observer and the microscopes cut off any disturbing influence from the near approach of the observer's body.

(3) The microscopes themselves, and the carriages upon which they were mounted, were connected by carefully selected invar bars of negligible expansion coefficient.

(4) The faithful agreement of all the measurements on the standard brass bar before and after the many heatings left no reason for suspecting such a variation in the cross-hair distance.

Notwithstanding these conditions, it appeared to Chappuis that some positive proof should be offered that the distance between the cross-hairs remained unchanged while the heating was going on, inasmuch as all the measurements were made in terms of this distance. Accordingly, at his

[1] The new bulb, as well as the bar, were made with the utmost care by Dr. Heraeus, of Hanau, Germany, for this investigation.

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suggestion, it was arranged to retain a standard unheated bar in the field of the microscopes throughout the readings, so that the distance between the cross-hairs would be subject to check at any time during the observations. The arrangement made for the purpose is very simple and effective, as can be seen from the neighboring diagram (Fig. 11). The last two series of measurements were made with this appliance, and the fixed distance was found to remain constant throughout the series to within 0.003 mm., although on first setting up the apparatus a gradual adjustment of strain, amounting to 0.012 mm., took place during the first two days.

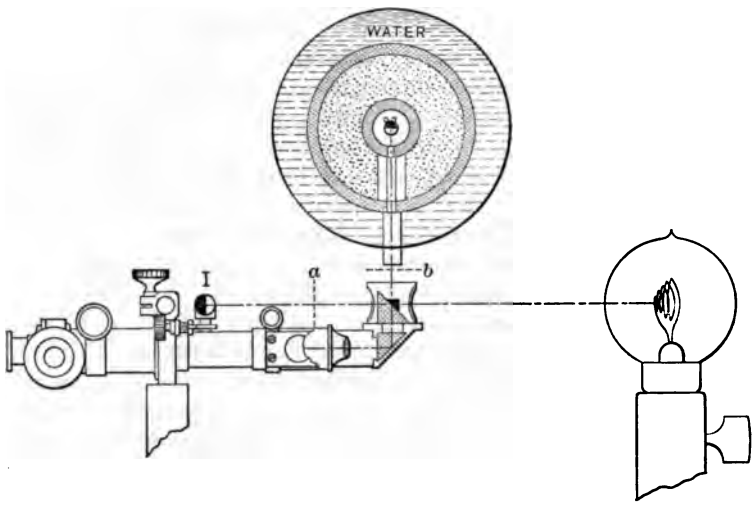


FIG. 11. A transverse section of the expansion-coefficient furnace at one of the openings, showing the method of illumination of the heated bar and the standard cold bar (I) together with an arrangement for checking the distance apart of the cross-hairs at each temperature. With a screen inserted at *a*, only the hot bar is visible; with the screen at *b*, only the cold bar. Compare with Fig. 6, p. 29.

The determination of $\beta$ is subject to two errors: The first is uncertainty of temperature, the second occurs in the measurement of the change in length. It was impossible to wind the furnace (70 cm. long and 1.5 cm. inside diameter, with two side openings) so as to give a perfectly uniform temperature along the bar; but as the furnace winding and consequent distribution of temperature were varied considerably for each run, the uncertainty from this cause was eliminated in the average of all the observations. The error in the temperature measurement itself was probably not over 2°, which would give an error of less than 0.2 per cent at the highest temperature. Two thermo-elements with a common junction were used, one entering from each end of the furnace. This not only gave a second temperature reading in confirmation of the first, but a positive check upon the appearance of contamination in the thermo-elements.[1]

With a half-meter bar and a temperature interval extending from zero to 1400°, the total expansion amounts to about 7.8 mm. The micrometers reading the expansion were read with an accuracy of 0.002 mm.

There was again some indication of a small hysteresis in the expansion and contraction. Although the amount was not much greater than the

[1]See p. 23.

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experimental error, the measurements indicate that the bar was slightly shorter after each heating than before, and that it gradually regained its original length. (See also p. 35.)

The measurements at room temperature are given in Table VIII. The five measurements in this table which were made within a few hours after the bar had cooled from a high temperature, excluding the two where the

TABLE VIII.—LENGTH OF PLATINUM-RHODIUM BAR.

| Date. | Maximum preceding temperature | Length at 0°. | Date. | Maximum preceding temperature. | Length at 0°. |
|---|---|---|---|---|---|
| 1 July 1908 | (New) | 500.068 | 26 Sept. 1908 | 1150° | 500.094 |
| 6 July 1908 | 900° | 500.110[1] | 1 Oct. 1908 | 25 | 500.119 |
| 9 July 1908 | 28 | 500.105 | 6 Oct. 1908 | 1300 | 500.034[2] |
| 13 July 1908 | 900 | 500.098[1] | 27 Oct. 1908 | 900 | 500.108[1] |
| 17 Sept. 1908 | 900 | 500.108[1] | 30 Oct. 1908 | 1400 | 500.096 |
| 19 Sept. 1908 | 1200 | 500.090 | 6 Oct. 1909 | 28 | 500.103 |
| 20 Sept. 1908 | 23 | 500.105 | 12 Oct. 1909 | 22 | 500.108[1] |
| 22 Sept. 1908 | 1200 | 500.087 | 13 Oct. 1909 | 1000 | 500.109 |
| 24 Sept. 1908 | 24 | 500.096 | 15 Oct. 1909 | 1400 | 500.074[2] |

bar was bent, average 500.095; while the ten measurements (excluding the first) which were made two days or more after heating average 500.106. The difference is only 0.002 per cent of the total length, or 0.12 per cent of the total expansion to 1500°, or about 0.7 per cent of the expansion to 300°. This effect is, therefore, probably responsible for the observed irregularities between 0° and 300°, at which point most of the temperature measurements were begun.[3]

## THE THERMO-ELECTRIC MEASUREMENTS.

The electromotive forces of the elements attached to the bulb were measured with a Wolff potentiometer. The standard of electromotive force used was the international volt, in terms of which the E. M. F. of the Clark cell is 1.4328 at 15°, and of the saturated cadmium cell used is 1.01835 volts at 25°.

Several small corrections are necessary in order to obtain the true E. M. F. of the thermo-element. The calibration corrections of the potentiometer (Reichsanstalt calibration) were all negligible except that for the fixed resistance to which the standard cell was attached. This correction amounted to 1.3 microvolts in 10,000. The correction for the change of resistance with temperature of the potentiometer was also negligible. The E. M. F. of the standard cell varies with the temperature; hence, the temperature of the cell was read at each measurement and a small correction applied. The readings were correct at 21.5°. For a variation of 5° from this temperature the correction was 2.2 microvolts in 10,000 microvolts. The resistance of the contacts of the potentiometer, and the small E. M. F.'s existing at contact points in the circuit of the thermo-element, introduced

[1] After interval of 4 to 7 days.
[2] After heating beyond the last temperature at which measurements were made it was discovered that the bar had become bent by sagging under its own weight.
[3] Kammerlingh-Onnes (Konink. Ak. Wet. Amsterdam, Proc., **10**, 342, 1907) has found the same effect after cooling platinum to very low temperatures.

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another small error which was determined by placing the thermo-element in ice and reading the E. M. F. This correction varied for the different elements from $-1$ to $+4$ microvolts.

As a check upon the absolute value, a Weston standard cadmium cell (calibration by the Bureau of Standards) whose E. M. F. was read directly on the potentiometer, was compared with the saturated cell each day. The agreement of the corrected values was usually within 0.5 microvolt. As in the case of the pressure measurement, the absolute value of the E. M. F. is not of importance, since it is used only for transference from the fixed points to the gas thermometer; the above corrections were applied, however, to reduce the readings to a common standard.

The effect of contamination (p. 23) of the thermo-element wires in furnace readings was much greater than the above-mentioned errors.[1] Up to 1100° the contamination was not serious, but above that temperature the wires take up iridium together with some rhodium. It was hoped that the replacement of iridium in the bulb by rhodium, which is much less volatile, would do away with this error, but there appeared still to be a very small percentage of iridium or other contaminating substance in the furnace or in the furnace wire, enough to affect the thermo-element wires appreciably, even though this furnace wire had been especially purified for this purpose.

Although the task became much longer and more laborious, it was thought wise to avoid the error from contamination, even of this diminished magnitude, rather than to attempt to compromise with it by any scheme of approximate evaluation. Accordingly, after every exposure of sufficient length to endanger the thermo-electric readings, all the thermo-elements were removed from the furnace and their wires tested for homogeneity. Where contamination was found, the contaminated portion of the wire was at once cut off. This is the only absolutely safe method of avoiding errors from this cause, for it amounts to the use of new thermo-elements exclusively in all the determinations of temperature distribution within the furnace as well as for establishing the absolute temperature of the metal melting-points.

*Testing the Thermo-element Wires.*—A very simple method of testing the wires for contamination has been developed, which consists in connecting the junction end of the wire to be tested, together with an uncontaminated wire, to the potentiometer and moving the free end of the standard wire along the wire to be tested, while heating the contact point of the two with a blast lamp.[2] The variation of the E. M. F. produced at this junction indicates the degree of contamination of the wire; in the uncontaminated portion this E. M. F. is small and constant within 3 microvolts. The temperature obtained by the blast-lamp flame is sufficiently constant for the purpose and lies between 1460° and 1500°.

The wires could be relied upon to give a constant E. M. F. within 3 microvolts at 1000° over a length of at least 50 cm, so that redeterminations of the fixed points were not necessary after cutting off each small portion of contaminated wire. Each test for contamination was continued over the 50 cm. of wire adjacent to the hot junction and so served as a test for the

[1] For a more thorough discussion of this effect, see W. P. White, Phys. Rev., **23**, 449–474, 1906.
[2] W. P. White, loc. cit., p. 454.

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homogeneity of the new wire which replaced the portion cut off. In two cases a sudden change of E. M. F. along the unused wire amounting to about 10 microvolts showed the probable presence of a junction point in the original sample from which the wire was drawn. Such a junction point was of course not introduced into the heated portion of the furnace.

In this connection, it should be pointed out that the relative weight to be given to the element inside the bulb, as compared with the outside elements, is greater at temperatures above 1100° than at temperatures below, for two reasons:

(1) The temperature at the middle of the bulb is not so much influenced above 1100° by the temperature of the lower part of the furnace as it is below 1100°.

(2) The outside elements are much more subject to contamination than the inside element by reason of the protection afforded the inside element by the intervening bulb walls against contaminating material from the heating coils or the furnace.

This is well shown by the data in Table XV, p. 105, on the melting-points of diopside, nickel, and cobalt. In the first measurements of these temperatures, the elements were left on the bulb through several runs, in consequence of which the readings of the outside elements on the bulb steadily decreased, whereas the temperatures derived from the inside elements are fairly constant. The contamination of the inside element was found to be less in amount and distributed over a region of more constant temperature.

For insulating the thermo-element wires from the bulb and furnace, capillary tubes, both of Marquardt porcelain and of silica glass, were employed. The Marquardt tubes are open to the objection that they are very porous and offer little protection against contamination. The silica glass capillaries protected the wires very much better, but at 1100° and above they devitrified rapidly and at the end of a measurement at 1400° or over fell from the wires in small fragments, so that the wires had to be taken off and reinsulated after a single run.

For the convenience of others who may confront similar problems, it may be added that such extreme precautions as cutting off the elements at the first sign of contamination are excessive for most purposes. The region of highest temperature, and therefore of most rapid contamination in a good furnace, is also a region of constant temperature. Contamination would therefore produce little effect upon the reading of the thermo-element until it had crept out into the colder parts of the furnace, which it will do slowly during long exposures. The distribution of the contamination in an aggravated case is shown in the table on page 66, which is arranged in such a way that not only the magnitude of the contamination but also its distribution with respect to the bulb is roughly shown. The electromotive forces are determined, as has been explained, by bringing successive points of the contaminated wire into contact with an uncontaminated one in a blast flame (temperature, 1460°–1500°), the cold junction being maintained constant at 0°. The absolute magnitude of the numbers in the column "before exposure" represents the electromotive force between two uncontaminated platinum wires of (nominally) equal purity. Its constant value is a measure of the homogeneity of the new wire. Its

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departure from this constant value "after exposure" is a measure of the contamination it has received. Slight irregularities are the result of variations in the blast-flame temperature. Such observations merely serve to furnish information about the distribution and approximate amount of contamination received by the element, but do not of themselves provide the data to correct its reading in a particular case.

It was found desirable to glow the thermo-elements occasionally by sending through them a current of from 12 to 17 amperes, depending upon the size of the wire. The glowing served to clean, soften, and straighten the wires, but did not affect the permanent electro-motive force of the element if not too long continued. The electro-motive force of a new element, however, was found to change on heating by as much as 10 micro-volts in 10,000. Elements made from freshly drawn wire were therefore always glowed for 5 minutes before they were calibrated and used.

| | Centi-meters from hot junction. | Before exposure (micro-volts). | After exposure (micro-volts). |
|---|---|---|---|
| | 40 | −4 | − 4 |
| | 35 | −6 | − 8 |
| Outside of furnace..... | 30 | −8 | − 7 |
| | 25 | −9 | − 6 |
| Bend of stem..... | 20 | −6 | −10 |
| | 15 | −5 | − 3 |
| | 12 | −5 | + 2 |
| | 10 | −5 | + 9 |
| Shoulder of bulb..... | 8 | −5 | +83 |
| | 6 | −5 | +83 |
| | 4 | −6 | +41 |
| | 2 | −6 | +55 |
| Middle of bulb..... | 0 | −8 | ..... |

*Integration of Temperatures over the Bulb.*—By the method which has been already described (p. 54), the differences of temperature between the ends of the bulb and the middle were determined differentially by means of platinum wires attached to the bulb itself. Temperatures about the circumference were measured by separate thermo-elements, as it was not practicable to measure these differences differentially because of the necessity of passing a platinum binding wire around the bulb to hold the four elements in position. A check on the accuracy of this differential method was obtained by using in one case a thermo-element at the top shoulder of the bulb and thus measuring the temperature at this point both directly and differentially by means of the platinum wire of this element. The two temperatures agreed within 0.8° when the deviation from the middle was 6°; when the temperatures at the middle and top were nearly equal, the two methods agreed to 0.1°.

Table IX contains approximate values of $\frac{\Delta e}{\Delta t}$, the rate of change of E. M. F. with temperature, at various temperatures from 400° to 1500°, both for the 10 per cent rhodium alloy and for the 20 per cent alloy of which the bulb was made. The data for the 20 per cent alloy (which need be only approximate) were obtained by two methods:

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(1) An element was made up by combining a platinum wire with the 20 per cent rhodium bar used for the expansion coefficient determination, and its readings were compared directly with those of a 10 per cent rhodium element in the melting-point furnace.

(2) A platinum wire was connected from the stem of the gas-thermometer bulb outside of the furnace to the ice box, and the E. M. F. determined against the standard platinum wire attached to the middle of the bulb. In both cases the E. M. F. of the junction of platinum with the rhodium alloy at room temperature was applied as a correction.

TABLE IX.—VALUES OF $\frac{\Delta e}{\Delta t}$ FOR THE ALLOYS 90 PT 10 RH AND 80 PT 20 RH.

| Temperature. | 90 Pt 10 Rh (microvolts per 1°). | 80 Pt 20 Rh (microvolts per 1°) |
|---|---|---|
| ° | | |
| 400 | 9.5 | 11.5 |
| 600 | 10.2 | 12.8 |
| 800 | 10.8 | 14.2 |
| 1000 | 11.5 | 15.6 |
| 1200 | 11.9 | 16.9 |
| 1400 | 12.1 | 17.5 |
| 1500 | 12.1 | 17.8 |

In order to obtain the true E. M. F. corresponding to the temperature as measured by the pressure of the gas in the bulb, it is necessary to integrate the various readings over the surface of the bulb. The following arbitrary weights were given to the different positions of elements on the surface:

| | |
|---|---|
| Top axis (position 1) | 5 |
| Top shoulder (position 2) | 20 |
| Middle (4 elements) (position 4) | 55 |
| Bottom shoulder (position 6) | 15 |
| Bottom axis (position 7) | 5 |

The elements on the axis at both top and bottom, although sometimes deviating from the others, have comparatively small weight, as they affect only a small portion of the total volume. The element at the lower shoulder of the bulb is given less weight than that at the top because of the smaller volume of the lower half, due to the presence of the reentrant tube.

It was easy to show experimentally that it matters very little what these relative weights assigned to the different readings may be, since the total correction was always small. In a number of cases, two different settings of the temperature distribution were made at each temperature, one in which the elements at the top and bottom shoulders of the bulb were made equal to the middle, and one in which the elements at top and bottom on the axis of the cylinder were made equal to the middle. The pressures corresponding to these two settings, reduced to the same reading of the standard element, are shown for several typical cases in the table below.

| Date. | Temperature. | Pressure when 1, 4 and 7 were equal. | Pressure when 2, 4 and 6 were equal. |
|---|---|---|---|
| | ° | *mm.* | *mm.* |
| 22 January, 1909 | 1082 | 1038.82 | 1038.64 |
| 2 July, 1909 | 1395 | 1285.43 | 1285.17 |
| 17 September, 1909 | 1489 | 1331.40 | 1330.63 |

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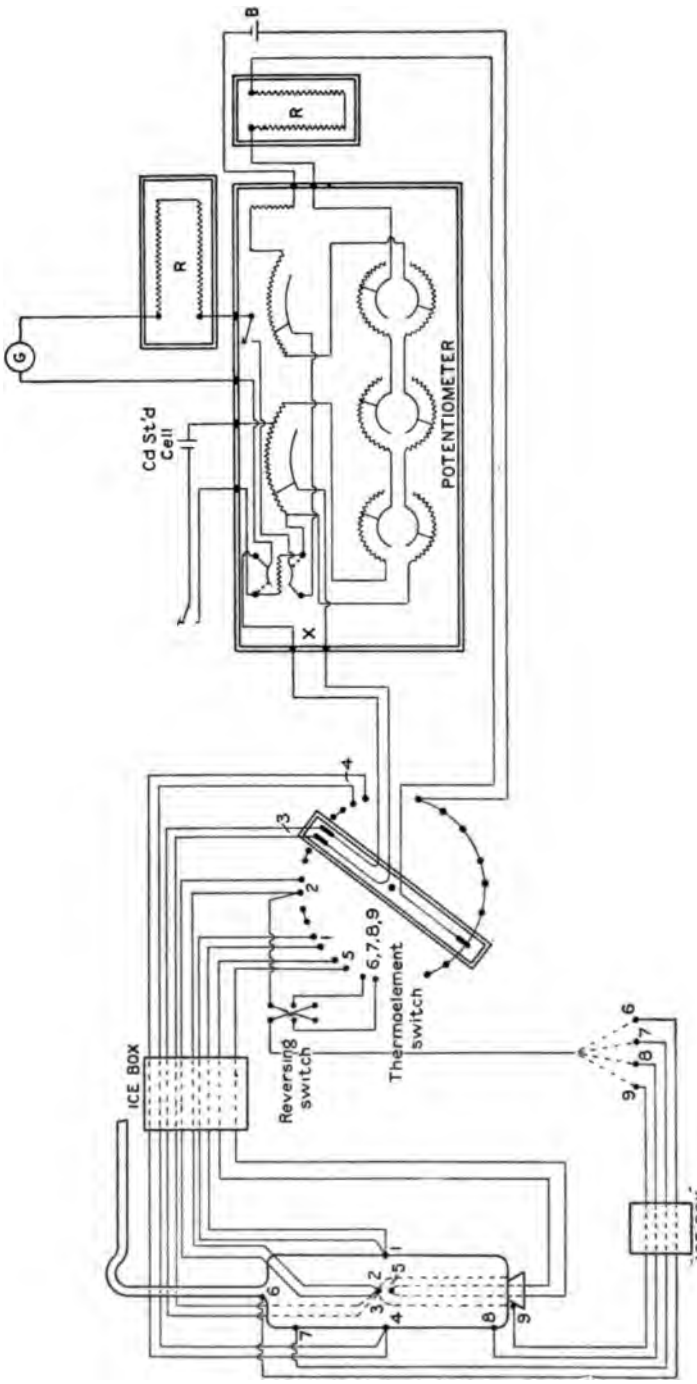


FIG. 12. Diagram of thermo-element connections from the gas-thermometer bulb to the potentiometer.

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It is evident that even without any correction for the different distribution in the two cases, the readings agreed within 0.2 to 0.8 mm. or about 0.2 to 0.9°, so that the variation between any two arbitrary sets of weights which might be given to the different readings must lie well within this limit.

The thermo-element connections, from the gas-thermometer bulb to the potentiometer, are shown diagrammatically in Fig. 12.

## SUMMARY OF THE ERRORS.

The effect on the final temperature of all the errors and corrections which have been discussed in this section is shown in summarized form in Table X. The figures of this table serve to emphasize the statements already

TABLE X.—ESTIMATED ERRORS AND THEIR EFFECT ON THE VALUE OF $t$.

| Quantity affected. | Source of error. | Amount of error. | | Effect on $t$. | |
|---|---|---|---|---|---|
| | | At 400°. | At 1500°. | At 400°. | At 1500°. |
| (A) Temperature of gas. | Temperature differences over bulb surface | 2 mv. | 5 mv. | ±0.2° | ±0.4° |
| | Variability | 0 | 1 mv. | 0 | ±0.1° |
| (B) $p_0$ | Reference point | 0.02 mm. | 0.02 mm. | ±0.04° | ±0.15° |
| $p_0$ | Manometer setting | 0.02 mm. | 0.02 mm. | ±0.04° | ±0.15° |
| $p_0$ | Scale corrections | 0.01 mm. | 0.01 mm. | ±0.02° | ±0.07° |
| $p_0$ | Temp. of mercury | 0.03 mm. | 0.03 mm. | ±0.06° | ±0.23° |
| $p_0$ | Barometer setting | 0.03 mm. | 0.03 mm. | ±0.06° | ±0.23° |
| $p_0$ | Temp. of barometer | 0.03 mm. | 0.03 mm. | ±0.06° | ±0.23° |
| $p_0$ | Variations in $p_0$ | 0 | 0–.05mm. | 0 | 0 to ±0.3° |
| $p$ | Reference point | 0.02 mm. | 0.02 mm. | ±0.02° | 0 |
| $p$ | Manometer setting | 0.02 mm. | 0.02 mm. | ±0.02° | 0 |
| $p$ | Scale corrections | 0.02 mm. | 0.02 mm. | ±0.02° | 0 |
| $p$ | Temp. of mercury | 0.07 mm. | 0.20 mm. | ±0.07° | ±0.05° |
| $p$ | Barometer setting | 0.03 mm. | 0.03 mm. | ±0.03° | ±0.01° |
| $p$ | Barometer temp. | 0.03 mm. | 0.03 mm. | ±0.03° | ±0.01° |
| $p$ | Unheated space $v_1$ | 0.020 cc. | 0.020 cc. | ±0.07° | ±0.5° |
| | Unheated space $t_1$ | 0.5–50° | 0.5°–100° | ±0.01° | ±0.1° |
| $\beta$ | Temperature | 1.0° | 2.0° | ±0.02° | ±0.11° |
| $\beta$ | Expansion | 0.005mm. | 0.008mm. | ±0.02° | ±0.09° |
| $\beta$ | Hysteresis in expansion | 0.01 mm. | 0.01 mm. | ±0.04° | ±0.10° |
| (C) E. M. F. | Instrumental correct'ns | 1 mv. | 2 mv. | ±0.1° | ±0.2° |
| E. M. F. | Contamination | 0 | 0–12 mv. | 0 | 0 to +1.0° |
| E. M. F. | Integration over bulb | 3 mv. | 12 mv. | ±0.3° | ±1.0° |
| (D) Fixed points | Instrumental correct'ns | 1 mv. | 2 mv. | ±0.1° | ±0.2° |
| Fixed points | Contamination | 0 | 0–10 mv. | 0 | 0 to −1.0° |
| Fixed points | Variation in given charge | Specific, | 1–10 mv. | Specific, | 0.1° to 1.0° |
| Fixed points | Variation between different charges | Specific, | 1–20 mv. | Specific, | 0.1° to 2.0° |

made, that the greatest present uncertainty in the high-temperature gas scale arises from the lack of uniformity in an air bath, which not only leads to uncertainty as to what is the true temperature of the gas in the bulb, but also to errors in the transference by the thermo-element. The next

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largest uncertainty, due to the limitations in the purity and reproducibility of the substances available for fixed points, is not directly chargeable to the gas thermometer. In this connection, considerable more work needs to be done on the high thermometric points, comparable in thoroughness to the work in low-temperature thermometry of Richards, Dickinson, and others, on the sodium sulphate transition-point.

## 13. EXPERIMENTAL DATA AND CALCULATED RESULTS.

### EXPANSION COEFFICIENT OF PLATINUM-RHODIUM.

In Table XI are given the experimental data on the expansion coefficients of the alloy 80 per cent platinum, 20 per cent rhodium. In the first column is given the date of the series, in the second and third columns the readings of the thermo-elements at the middle of the bar, corrected for zero error and the temperature of the cadmium cell. The 12 other readings taken with each element at each temperature at different points along the bar can not be given here,[1] but the fourth and fifth columns contain the readings of the thermo-element corrected to represent the integrated temperature along the bar. For convenience, the integration was made in terms of microvolts instead of degrees. The sixth and seventh columns contain the temperatures corresponding to the readings in columns 4 and 5, and the eighth column contains the mean of these two temperatures. The micrometer readings are not given, but in column 9 will be found the expansions reduced to millimeters for that portion of the bar lying between the 0 and 50 cm. marks on the ends. Each of these represents the mean of eight settings at each end of the bar. In the last column are given the values of the mean expansion coefficient from 0°, calculated by dividing the expansion by the length at 0° and by the temperature.

For convenience of comparison, the values of $\beta$ at the nearest round temperatures were interpolated linearly between the observations in each series, and the results are given in Table XII. Values interpolated between these values are given in parentheses.

The table shows that the percentage error at 300° is greater than that at 1200° and above, probably on account of the larger effect of the hysteresis in the expansion and contraction, already discussed on page 63. The agreement of the results is very satisfactory, particularly in view of the fact that each series represents an entirely different curve of temperature variation along the bar. In some cases the temperatures at the end were lower than at the middle, in others higher than at the middle, and in one series one end was higher and the other lower. The mean of all, therefore, probably eliminates any error which might arise from variation of temperature along the bar.

The results are represented within the limits of error by the straight-line equation

$$10^6\beta = 8.79 + 0.00161t$$

[1] See p. 36 for an example of such readings, showing distribution of temperature in the case of the platinum-iridium bar.

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This may be compared here with the expansion coefficients between 300° and 1000° determined by the authors for the 10 per cent iridium alloy,[1] and by Holborn and Day[2] for the 20 per cent iridium alloy and for pure platinum:

80 Pt 20 Ir, $10^6\beta = 8.20 + 0.00142t$
90 Pt 10 Ir, $10^6\beta = 8.84 + 0.00131t$
Pt, $10^6\beta = 8.87 + 0.00132t$

TABLE XI.—OBSERVATIONS OF EXPANSION COEFFICIENT, $\beta$.

| Date. | Thermo elements. | | | | Temperature. | | | Expansion from 0°. | |
|---|---|---|---|---|---|---|---|---|---|
| | W | Z | W cor. | Z cor. | By W | By Z | Mean. | Millimeters on 500 mm. | $10^6\beta$ |
| 1908. | | | | | ° | ° | ° | | |
| Sept. 21.... | 2261 | 2251 | 2312 | 2298 | 301.4 | 301.4 | 301.4 | 1.404 | 9.32 |
| | 3197 | 3187 | 3273 | 3258 | 404.6 | 405.4 | 405.0 | 1.912 | 9.44 |
| | 4169 | 4153 | 4257 | 4237 | 506.0 | 507.1 | 506.6 | 2.434 | 9.61 |
| | 5157 | 5140 | 5237 | 5212 | 603.9 | 605.1 | 604.5 | 2.950 | 9.76 |
| | 6197 | 6178 | 6286 | 6262 | 705.4 | 707.2 | 706.3 | 3.500 | 9.91 |
| | 7264 | 7238 | 7362 | 7333 | 806.2 | 807.8 | 807.0 | 4.064 | 10.07 |
| | 8361 | 8335 | 8457 | 8420 | 905.9 | 906.7 | 906.3 | 4.640 | 10.24 |
| | 9509 | 9470 | 9599 | 9552 | 1006.9 | 1006.8 | 1006.8 | 5.241 | 10.41 |
| | 10662 | 10611 | 10733 | 10675 | 1104.5 | 1103.4 | 1104.0 | 5.828 | 10.56 |
| | 11963 | 11896 | 12018 | 11921 | 1215.3 | 1210.2 | 1212.8 | 6.469 | 10.67 |
| Sept. 25.... | 1817 | 1801 | 1848 | 1831 | 248.7 | 248.4 | 248.6 | 1.154 | 9.28 |
| | 2756 | 2735 | 2791 | 2768 | 353.4 | 352.9 | 353.2 | 1.666 | 9.43 |
| | 3699 | 3674 | 3726 | 3702 | 451.8 | 452.0 | 451.9 | 2.158 | 9.55 |
| | 4686 | 4655 | 4691 | 4662 | 549.7 | 550.3 | 550.0 | 2.668 | 9.70 |
| | 5711 | 5679 | 5691 | 5660 | 648.2 | 649.2 | 648.7 | 3.191 | 9.84 |
| | 6820 | 6788 | 6772 | 6742 | 751.2 | 752.6 | 751.9 | 3.757 | 9.99 |
| | 7847 | 7813 | 7754 | 7720 | 842.2 | 843.2 | 842.7 | 4.262 | 10.11 |
| | 8980 | 8945 | 8845 | 8809 | 940.8 | 941.4 | 941.1 | 4.827 | 10.26 |
| | 10140 | 10102 | 9939 | 9901 | 1036.4 | 1037.0 | 1036.8 | 5.403 | 10.42 |
| | 11368 | 11327 | 11109 | 11063 | 1136.9 | 1136.4 | 1136.7 | 6.012 | 10.58 |
| Oct. 3..... | 2291 | 2272 | 2302 | 2283 | 300.3 | 299.8 | 300.1 | 1.384 | 9.22 |
| | 3228 | 3205 | 3250 | 3228 | 402.2 | 402.2 | 402.2 | 1.899 | 9.44 |
| | 4208 | 4181 | 4243 | 4215 | 504.6 | 504.9 | 504.8 | 2.432 | 9.63 |
| | 5205 | 5175 | 5247 | 5216 | 604.8 | 605.5 | 605.2 | 2.964 | 9.79 |
| | 6238 | 6206 | 6281 | 6249 | 704.9 | 705.9 | 705.4 | 3.511 | 9.95 |
| | 7297 | 7263 | 7342 | 7309 | 804.4 | 805.5 | 805.0 | 4.069 | 10.11 |
| | 8401 | 8365 | 8446 | 8408 | 904.9 | 905.6 | 905.3 | 4.644 | 10.26 |
| | 9536 | 9497 | 9576 | 9534 | 1004.9 | 1005.2 | 1005.1 | 5.231 | 10.41 |
| | 10675 | 10647 | 10710 | 10670 | 1102.6 | 1103.0 | 1102.8 | 5.830 | 10.57 |
| | 11884 | 11857 | 11926 | 11875 | 1207.5 | 1206.2 | 1206.8 | 6.466 | 10.71 |
| Oct. 29..... | 8419 | 8377 | 8366 | 8324 | 897.4 | 898.0 | 897.7 | 4.618 | 10.29 |
| | 9551 | 9507 | 9436 | 9392 | 992.6 | 992.8 | 992.7 | 5.169 | 10.41 |
| | 10706 | 10663 | 10539 | 10496 | 1088.0 | 1088.2 | 1088.1 | 5.752 | 10.57 |
| | 11884 | 11849 | 11786 | 11751 | 1195.6 | 1195.7 | 1195.7 | 6.401 | 10.70 |
| | 13137 | 13104 | 13134 | 13101 | 1309.9 | 1309.8 | 1309.9 | 7.154 | 10.92 |
| 1909. | W | D | W cor. | D cor. | By W | By D | | | |
| Oct. 13..... | 2304 | 2301 | 2235 | 2232 | 293.0 | 293.0 | 293.0 | 1.352 | 9.23 |
| | 6222 | 6217 | 6180 | 6175 | 695.2 | 695.9 | 695.6 | 3.452 | 9.92 |
| | 9501 | 9494 | 9493 | 9486 | 997.6 | 998.1 | 997.9 | 5.190 | 10.40 |
| Oct. 14..... | 9540 | 9536 | 9542 | 9544 | 1001.9 | 1003.1 | 1002.5 | 5.200 | 10.37 |
| | 10666 | 10663 | 10690 | 10691 | 1101.9 | 1102.5 | 1102.2 | 5.811 | 10.54 |
| | 11839 | 11836 | 11783 | 11783 | 1195.4 | 1195.7 | 1195.6 | 6.410 | 10.72 |
| | 12998 | 12993 | 13121 | 13120 | 1308.9 | 1308.6 | 1308.8 | 7.156 | 10.93 |
| | 14183 | 14170 | 14390 | 14372 | 1413.4 | 1411.6 | 1412.5 | 7.832 | 11.09 |

[1] See pp. 27–39.
[2] Am. Jour. Sci. (4), 11, 374–390, 1901. Ann. d. Phys. (4), 4, 104–122, 1901.

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TABLE XII.—VALUES OF $10^6\beta$ AT ROUND TEMPERATURES FOR THE ALLOY 80 PT 20 RH.

| Temp. | 21 Sept. 1908. | 25 Sept. 1908. | 3 Oct. 1908. | 29 Oct. 1908. | 13 Oct. 1909. | 14 Oct. 1909. | Mean. |
|---|---|---|---|---|---|---|---|
| 250 | ..... | 9.28 | ..... | ..... | ..... | ..... | ..... |
| 300 | 9.31 | (9.36) | 9.22 | ..... | 9.24 | ..... | 9.28 |
| 350 | (9.37) | 9.43 | (9.33) | ..... | (9.33) | ..... | 9.36 |
| 400 | 9.43 | (9.49) | 9.44 | ..... | (9.41) | ..... | 9.44 |
| 450 | (9.52) | 9.55 | (9.53) | ..... | (9.50) | ..... | 9.52 |
| 500 | 9.60 | (9.62) | 9.62 | ..... | (9.58) | ..... | 9.61 |
| 550 | (9.67) | 9.70 | (9.71) | ..... | (9.67) | ..... | 9.69 |
| 600 | 9.75 | (9.77) | 9.79 | ..... | (9.76) | ..... | 9.77 |
| 650 | (9.83) | 9.84 | (9.86) | ..... | (9.84) | ..... | 9.84 |
| 700 | 9.90 | (9.92) | 9.94 | ..... | 9.93 | ..... | 9.92 |
| 750 | (9.98) | 9.99 | (10.02) | ..... | (10.01) | ..... | 10.00 |
| 800 | 10.06 | (10.06) | 10.10 | ..... | (10.09) | ..... | 10.08 |
| 850 | (10.14) | 10.12 | (10.17) | ..... | (10.16) | ..... | 10.15 |
| 900 | 10.23 | (10.20) | 10.25 | 10.29 | (10.24) | ..... | 10.24 |
| 950 | (10.31) | 10.27 | (10.32) | (10.36) | (10.32) | ..... | 10.32 |
| 1000 | 10.40 | (10.36) | 10.40 | 10.42 | 10.40 | 10.37 | 10.39 |
| 1050 | (10.47) | 10.44 | (10.48) | (10.50) | ..... | (10.45) | 10.47 |
| 1100 | 10.55 | (10.52) | 10.57 | 10.59 | ..... | 10.54 | 10.55 |
| 1150 | (10.60) | 10.60 | (10.64) | (10.65) | ..... | (10.63) | 10.62 |
| 1200 | 10.65 | (10.67) | 10.71 | 10.71 | ..... | 10.73 | 10.69 |
| 1250 | ..... | ..... | ..... | (10.81) | ..... | (10.82) | 10.81 |
| 1300 | ..... | ..... | ..... | 10.90 | ..... | 10.92 | 10.91 |
| 1350 | ..... | ..... | ..... | (10.99) | ..... | (10.99) | 10.99 |
| 1400 | ..... | ..... | ..... | ..... | ..... | 11.07 | 11.07 |
| 1450 | ..... | ..... | ..... | ..... | ..... | ..... | (11.15) |
| 1500 | ..... | ..... | ..... | ..... | ..... | ..... | (11.23) |

## GAS-THERMOMETER DATA.

In Table XIII are given the observed gas-thermometer data.[1] In the first column is the date of measurement. The measurements are numbered chronologically in the second column for convenience of reference. In the third column is the measured pressure, $p'$ (or $p_o'$), in millimeters of mercury at 0°, corrected as described on pages 57–58. The application of the correction for unheated space (see p. 58) gives the pressure $p$ (or $p_o$) which is found in the fourth column. In the fifth column is the value of the temperature, $t$, calculated by formula (5) on page 53. In column 6 are given the readings of the standard thermo-elements in microvolts, and in column 7 the positions of these elements on the bulb; for the significance of these figures see Fig. 8 and note on page 55. In the last column are given the other elements which were used on the bulb, together with their positions designated in the same way. The italicized letters represent single platinum wires instead of thermo-elements.

A few measurements in which the value of $p_o$ changed by more than 0.1 per cent have been omitted; their position is shown by the absence of their corresponding serial numbers.

[1] For the measurements in the table, seven furnaces were employed, using three different coils of platinum wire of about 400 grams each. One of these furnaces was wound on the outside, the other six on the inside of the tube. It was possible to rewind the wire at least once after the furnace had burned out. Failure always occurred several centimeters away from the bulb in the end portions of the furnace, which, in order to secure uniformity of temperature over the bulb, had to be considerably superheated. Only one measurement was made at the palladium point, as this one rendered the furnace unfit for further use; the conditions of this measurement were, however, perfect.

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TABLE XIII.—OBSERVED GAS-THERMOMETER DATA.

Gas Filling No. 1.

| Date. | No. | $p'$ (or $p_0'$) | $p$ (or $p_0$) | $t$ | Standard elements. | Position. | Other elements and positions. |
|---|---|---|---|---|---|---|---|
| 1908. | | | | | | | |
| 30 Nov..... | 1 | 217.65 | 217.63 | 0° | ..... | | |
| 30 Nov..... | 2 | 1037.77 | 1042.72 | 1079.87 | W 10443<br>X 10491 | 4<br>8 | Z (1), S (9) |
| 1 Dec..... | 3 | 217.45 | 217.43 | 0 | .... | | |
| 2 Dec..... | 5 | 217.10 | 217.08 | 0 | .... | | |
| 3 Dec..... | 6 | 948.81 | 952.84 | 960.59 | W 9061<br>X 9100 | 4<br>8 | Z (1), S (9) |
| 4 Dec..... | 7 | 217.12 | 217.10 | 0 | .... | | |
| 16 Dec..... | 8 | 217.08 | 217.06 | 0 | .... | | |
| 17 Dec..... | 9 | 1038.50 | 1043.48 | 1083.61 | W 10483<br>X 10555 | 4<br>8 | Z (1), S (9) |
| 18 Dec..... | 10 | 217.18 | 217.16 | 0 | .... | | |
| 19 Dec..... | 11 | 1038.57 | 1043.56 | 1083.77 | W 10473<br>X 10512 | 4<br>8 | Z (1), X (9) |
| 21 Dec..... | 12 | 217.06 | 217.04 | 0 | .... | | |
| 23 Dec..... | 15 | 217.49 | 217.47 | 0 | .... | | |
| 24 Dec..... | 16 | 1242.38 | 1249.71 | 1365.71 | A 13866<br>X .... | 4<br>8 | Y (1), S (9) |
| 28 Dec..... | 17 | 217.57 | 217.55 | 0 | .... | | |
| 1909. | | | | | | | |
| 22 Jan..... | 18 | 1039.78 | 1044.74 | 1082.84 | A 10502<br>Y 10612 | 4<br>8 | Z (9), *B* (1.3)<br>*W* (2.3), *S* (6.7)<br>*X* (7.3) |
| 22 Jan..... | 19 | 1038.82 | 1043.79 | 1081.87 | A 10506<br>Y 10584 | 4<br>8 | Do. |
| 22 Jan..... | 20 | 1037.85 | 1042.83 | 1080.89 | A 10498<br>Y 10555 | 4<br>8 | Do. |
| 23 Jan..... | 21 | 217.36 | 217.34 | 0 | .... | | |
| 25 Jan..... | 22 | 543.01 | 544.07 | 418.40 | A 3414<br>Y 3436 | 4.5<br>8 | Do. |
| 25 Jan..... | 23 | 542.27 | 543.32 | 417.43 | A 3408<br>Y 3435 | 4.5<br>8 | Do. |
| 26 Jan..... | 24 | 703.78 | 705.81 | 629.80 | A 5510<br>Y 5550 | 4.5<br>8 | Do. |
| 26 Jan..... | 25 | 702.64 | 704.67 | 628.34 | A 5501<br>Y 5529 | 4.5<br>8 | Do. |
| 26 Jan..... | 26 | 949.56 | 953.63 | 960.22 | A 9090<br>Y 9159 | 4.5<br>8 | Do. |
| 26 Jan..... | 27 | 948.15 | 952.23 | 958.41 | A 9075<br>Y 9119 | 4.5<br>8 | Do. |
| 26 Jan..... | 28 | 1039.03 | 1044.05 | 1083.01 | A 10515<br>Y 10593 | 4.5<br>8 | Do. |
| 26 Jan..... | 29 | 1037.92 | 1042.93 | 1081.56 | A 10505<br>Y 10556 | 4.5<br>8 | Do. |
| 27 Jan..... | 30 | 217.33 | 217.31 | 0 | .... | | |
| 28 Jan..... | 31 | 542.87 | 543.92 | 418.30 | A 3410<br>Y 3436 | 4.5<br>8 | Do. |
| 28 Jan..... | 32 | 542.07 | 543.11 | 417.25 | A 3404<br>Y 3425 | 4.5<br>8 | Do. |
| 28 Jan..... | 33 | 704.06 | 706.07 | 630.21 | A 5514<br>Y 5553 | 4.5<br>8 | Do. |
| 28 Jan..... | 34 | 703.35 | 705.37 | 629.31 | A 5510<br>Y 5537 | 4.5<br>8 | Do. |
| 28 Jan..... | 35 | 948.96 | 953.05 | 959.46 | A 9087<br>Y 9142 | 4.5<br>8 | Do. |
| 28 Jan..... | 36 | 949.86 | 953.97 | 960.69 | A 9098<br>Y 9163 | 4.5<br>8 | Do. |
| 28 Jan..... | 37 | 1038.50 | 1043.57 | 1082.23 | A 10511<br>Y 10576 | 4.5<br>8 | Do. |

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TABLE XIII—OBSERVED GAS-THERMOMETER DATA—Continued.

Gas Filling No. 1—Continued.

| Date. | No. | $p'$(or $p_0'$) | $p$(or $p_0$) | $t$ | Standard elements. | | Position. | Other elements and positions. |
|---|---|---|---|---|---|---|---|---|
| 1909. | | | | | | | | |
| 28 Jan..... | 38 | 1038.99 | 1044.06 | 1082.90 | A | 10512 | 4.5 | Z (9), B (1.3), W (2.3), S(6.7)X (7.3) |
| | | | | | Y | 10585 | 8 | |
| 28 Jan..... | 39 | 1039.61 | 1044.68 | 1083.68 | A | 10509 | 4.5 | |
| | | | | | Y | 10617 | 8 | Do. |
| 29 Jan..... | 40 | 217.37 | 217.35 | 0° | | .... | | |
| 29 Jan..... | 41 | 949.32 | 953.38 | 959.78 | A | 9086 | 4.5 | |
| | | | | | Y | 9156 | 8 | Do. |
| 29 Jan..... | 42 | 948.58 | 952.66 | 958.81 | A | 9085 | 4.5 | |
| | | | | | Y | 9131 | 8 | Do. |
| 29 Jan..... | 43 | 1039.29 | 1044.34 | 1083.15 | A | 10515 | 4.5 | |
| | | | | | Y | 10595 | 8 | Do. |
| 29 Jan..... | 44 | 1038.49 | 1043.56 | 1082.09 | A | 10511 | 4.5 | |
| | | | | | Y | 10568 | 8 | Do. |
| 29 Jan..... | 45 | 1039.63 | 1044.71 | 1083.58 | A | 10508 | 4.5 | |
| | | | | | Y | 10617 | 8 | Do. |
| 30 Jan..... | 46 | 217.39 | 217.37 | 0 | | .... | | |

Gas Filling No. 2.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1909. | | | | | | | | |
| 18 Feb..... | 47 | 346.74 | 346.70 | 0 | | .... | | |
| 22 Feb..... | 48 | 346.78 | 346.74 | 0 | | .... | | |
| | | | | | A | 2487 | 4.5 | W (1.3), B (2.2), |
| 23 Feb..... | 49 | 745.09 | 746.19 | 319.55 | D | 2483 | 4.5 | X (6.2), S (7.3), |
| | | | | | Z | 2462 | 8 | Y (12) |
| | | | | | A | 3414 | 4.5 | Do. |
| 23 Feb..... | 50 | 866.47 | 868.15 | 418.40 | D | 3406 | 4.5 | |
| | | | | | Z | 3385 | 8 | |
| | | | | | A | 4451 | 4.5 | Do. |
| 23 Feb..... | 51 | 995.97 | 998.38 | 524.71 | D | 4439 | 4.5 | |
| | | | | | Z | 4413 | 8 | |
| | | | | | A | 5510 | 4.5 | Do. |
| 23 Feb..... | 52 | 1122.39 | 1125.61 | 629.37 | D | 5495 | 4.5 | |
| | | | | | Z | 5463 | 8 | |
| 24 Feb..... | 53 | 346.67 | 346.63 | 0 | | .... | | |
| 26 Feb..... | 59 | 346.24 | 346.20 | 0 | | .... | | |
| | | | | | A | 10508 | 4.5 | W (3.3), B (2.2), |
| 26 Feb..... | 60 | 1657.03 | 1665.07 | 1083.17 | D | 10473 | 4.5 | X (6.2), S (7.2), |
| | | | | | Z | 10422 | 8 | Y (12) |
| 27 Feb..... | 61 | 346.45 | 346.41 | 0 | | .... | | |
| | | | | | A | 7895 | 4.5 | B (3.2), W (2.3), |
| 1 Mar..... | 62 | 1388.84 | 1394.13 | 853.76 | D | 7869 | 4.5 | X (6.2), S (7.2), |
| | | | | | Z | 7829 | 8 | Y (12) |
| | | | | | A | 9086 | 4.5 | Do. |
| 1 Mar..... | 63 | 1513.67 | 1520.20 | 960.29 | D | 9055 | 4.5 | |
| | | | | | Z | 9010 | 8 | |
| | | | | | A | 10265 | 4.5 | Do. |
| 1 Mar..... | 64 | 1632.03 | 1639.78 | 1062.15 | D | 10229 | 4.5 | |
| | | | | | Z | 10178 | 8 | |
| | | | | | A | 10511 | 4.5 | Do. |
| 1 Mar..... | 65 | 1655.77 | 1663.81 | 1082.84 | D | 10474 | 4.5 | |
| | | | | | Z | 10420 | 8 | |
| 2 Mar..... | 66 | 346.20 | 346.17 | 0 | | .... | | |
| | | | | | A | 7885 | 4.5 | W (3.3), B (2.2) |
| 3 Mar..... | 67 | 1386.28 | 1391.55 | 852.44 | D | 7861 | 4.5 | X (6.2), S (7.2) |
| | | | | | Z | 7820 | 8 | Y (12) |

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TABLE XIII.—OBSERVED GAS-THERMOMETER DATA—Continued.

Gas Filling No. 2—Continued.

| Date. | No. | $p'$ (or $p_0'$) | $p$ (or $p_0$) | $t$ | Standard elements. | | Position. | Other elements and positions. |
|---|---|---|---|---|---|---|---|---|
| 1909. | | | | | | | | |
| | | | | | A | 9088 | 4.5 | $W$ (3.3), $B$ (2.2), |
| 3 Mar..... | 68 | 1511.95 | 1518.48 | 959.81 | D | 9059 | 4.5 | $X$ (6.2), $S$ (7.2), |
| | | | | | Z | 9013 | 8 | Y (12) |
| | | | | | A | 10257 | 4.5 | Do. |
| 3 Mar..... | 69 | 1628.71 | 1636.46 | 1060.24 | D | 10221 | 4.5 | |
| | | | | | Z | 10169 | 8 | |
| | | | | | A | 10512 | 4.5 | Do. |
| 3 Mar..... | 70 | 1654.46 | 1662.50 | 1082.73 | D | 10478 | 4.5 | |
| | | | | | Z | 10444 | 8 | |
| 5 Mar..... | 71 | 345.98 | 345.94 | 0 | .... | | | |
| Gas Filling No. 3. | | | | | | | | |
| 1909. | | | | | | | | |
| 4 June..... | 72 | 345.31 | 345.27 | 0 | .... | | | |
| | | | | | A | 3403 | 4.1 | Y (1), $a$ (2.4), |
| | | | | | E | 3419 | 4.3 | $b$ (6.4) |
| 4 June..... | 73 | 861.67 | 862.94 | 417.07 | F | 3414 | 4.5 | |
| | | | | | G | 3416 | 4.7 | |
| | | | | | Z | 3370 | 8 | |
| | | | | | A | 5516 | 4.1 | Do. |
| | | | | | E | 5535 | 4.3 | |
| 4 June..... | 74 | 1118.50 | 1120.83 | 629.11 | F | 5528 | 4.5 | |
| | | | | | G | 5529 | 4.7 | |
| | | | | | Z | 5461 | 8 | |
| 5 June..... | 75 | 345.31 | 345.27 | 0 | .... | | | |
| | | | | | A | 9090 | 4.1 | Do. |
| | | | | | E | 9114 | 4.3 | |
| 5 June..... | 76 | 1510.50 | 1515.27 | 959.77 | F | 9099 | 4.5 | |
| | | | | | G | 9108 | 4.7 | |
| | | | | | Z | 9002 | 8 | |
| | | | | | A | 10258 | 4.1 | Do. |
| | | | | | E | 10285 | 4.3 | |
| 5 June..... | 77 | 1628.08 | 1633.64 | 1060.53 | F | 10266 | 4.5 | |
| | | | | | G | 10279 | 4.7 | |
| | | | | | Z | 10161 | 8 | |
| | | | | | A | 10503 | 4.1 | Do. |
| | | | | | E | 10529 | 4.3 | |
| 5 June..... | 78 | 1652.36 | 1658.10 | 1081.28 | F | 10510 | 4.5 | |
| | | | | | G | 10523 | 4.7 | |
| | | | | | Z | 10404 | 8 | |
| 7 June..... | 79 | 345.50 | 345.46 | 0 | .... | | | |
| 10 June..... | 80 | 345.52 | 345.48 | 0 | .... | | | |
| | | | | | F | 9120 | 4.1 | $a$ (1), $b$ (2.4), |
| | | | | | E | 9128 | 4.3 | $c$ (6.4), $e$ (7.3) |
| 18 June..... | 81 | 1512.96 | 1517.69 | 961.21 | A | 9080 | 4.5 | |
| | | | | | G | 9122 | 4.7 | |
| | | | | | Z | 9015 | 8 | |
| | | | | | F | 10299 | 4.1 | Do. |
| | | | | | E | 10300 | 4.3 | |
| 18 June..... | 82 | 1630.94 | 1636.53 | 1062.53 | A | 10252 | 4.5 | |
| | | | | | G | 10292 | 4.7 | |
| | | | | | Z | 10181 | 8 | |
| | | | | | F | 10534 | 4.1 | Do. |
| | | | | | E | 10534 | 4.3 | |
| 18 June..... | 83 | 1653.61 | 1659.37 | 1082.14 | A | 10487 | 4.5 | |
| | | | | | G | 10526 | 4.7 | |
| | | | | | Z | 10403 | 8 | |

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TABLE XIII.—OBSERVED GAS-THERMOMETER DATA—Continued.

Gas Filling No. 3—Continued.

| Date. | No. | $p'$ (or $p_0'$) | $p$ (or $p_0$) | $t$ | Standard elements. | Position. | Other elements and positions. |
|---|---|---|---|---|---|---|---|
| 1909. | | | | | | | |
| | | | | | F 10536 | 4.1 | *a* (1), *b* (2.4) |
| | | | | | E 10534 | 4.3 | *c* (6.4), *e* (7.3) |
| 18 June..... | 84 | 1654.51 | 1660.27 | 1082.91 | A 10485 | 4.5 | |
| | | | | | G 10525 | 4.7 | |
| | | | | | Z 10426 | 8 | |
| 19 June..... | 85 | 345.51 | 345.47 | 0 | .... | | |
| | | | | Gas Filling No. 3a. | | | |
| 1909. | | | | | | | |
| 19 June..... | 86 | 219.73 | 219.71 | 0 | .... | | |
| | | | | | F 5520 | 4.1 | *a* (1), *e* (2.3) |
| | | | | | E 5520 | 4.3 | *c* (6.3), *f* (7.3) |
| 19 June..... | 87 | 710.34 | 711.83 | 627.61 | A 5484 | 4.5 | |
| | | | | | G 5516 | 4.7 | |
| | | | | | Z 5437 | 8 | |
| | | | | | F 9139 | 4.1 | Do. |
| | | | | | E 9136 | 4.3 | |
| 19 June..... | 88 | 962.21 | 965.23 | 961.71 | A 9089 | 4.5 | |
| | | | | | G 9131 | 4.7 | |
| | | | | | Z 9036 | 8 | |
| | | | | | F 10540 | 4.1 | Do. |
| | | | | | E 10538 | 4.3 | |
| 19 June..... | 89 | 1051.74 | 1055.41 | 1082.75 | A 10490 | 4.5 | |
| | | | | | G 10532 | 4.7 | |
| | | | | | Z 10428 | 8 | |
| 21 June..... | 90 | 219.74 | 219.72 | 0 | .... | | |
| 22 June..... | 92 | 220.65 | 220.63 | 0 | .... | | |
| 24 June..... | 93 | 220.62 | 220.59 | 0 | .... | | |
| 25 June..... | 95 | 220.56 | 220.53 | 0 | .... | | |
| | | | | | H 14251 | 4.1 | Do. |
| | | | | | E 14227 | 4.3 | |
| 2 July..... | 96 | 1283.36 | 1288.82 | 1391.97 | F 14222 | 4.5 | |
| | | | | | G 14245 | 4.7 | |
| | | | | | Z 14121 | 8 | |
| | | | | | H 14282 | 4.1 | Do. |
| | | | | | E 14247 | 4.3 | |
| 2 July..... | 97 | 1285.43 | 1290.89 | 1394.89 | F 14241 | 4.5 | |
| | | | | | G 14274 | 4.7 | |
| | | | | | Z 14156 | 8 | |
| 3 July..... | 98 | 221.02 | 220.99 | 0 | .... | | |
| | | | | | H 14213 | 4.1 | Do. |
| | | | | | E 14214 | 4.3 | |
| 3 July..... | 99 | 1281.97 | 1287.45 | 1393.34 | F 14196 | 4.5 | |
| | | | | | G 14216 | 4.7 | |
| | | | | | Z 14099 | 8 | |
| | | | | | H 14264 | 4.1 | Do. |
| | | | | | E 14242 | 4.3 | |
| 3 July..... | 100 | 1284.05 | 1289.54 | 1396.17 | F 14235 | 4.5 | |
| | | | | | G 14259 | 4.7 | |
| | | | | | Z 14156 | 8 | |
| 6 July..... | 101 | 220.62 | 220.60 | 0 | .... | | |

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TABLE XIII.—OBSERVED GAS-THERMOMETER DATA—Continued.

Gas Filling No. 4.

| Date. | No. | $p'$ (or $p_o'$) | $p$ (or $p_o$) | $t$ | Standard elements. | Posi-tion. | Other elements and positions. |
|---|---|---|---|---|---|---|---|
| 1909 | | | | | | | |
| 8 July..... | 102 | 216.81 | 216.79 | 0 | .... | | |
| | | | | | H 14235 | 4.1 | *a* (1), *e* (2.3) |
| | | | | | E 14216 | 4.3 | *c* (6.3), *f* (7.3) |
| 8 July..... | 103 | 1261.35 | 1266.80 | 1391.15 | F 14209 | 4.5 | |
| | | | | | G 14222 | 4.7 | |
| | | | | | Z 14124 | 8 | |
| | | | | | H 14249 | 4.1 | Do. |
| | | | | | E 14229 | 4.3 | |
| 8 July..... | 104 | 1263.13 | 1268.59 | 1393.55 | F 14199 | 4.5 | |
| | | | | | G 14236 | 4.7 | |
| | | | | | Z 14155 | 8 | |
| 9 July..... | 105 | 217.36 | 217.33 | 0 | .... | | |
| | | | | | H 14251 | 4.1 | Do. |
| | | | | | E 14236 | 4.3 | |
| 9 July..... | 106 | 1261.71 | 1267.15 | 1391.64 | F 14233 | 4.5 | |
| | | | | | G 14241 | 4.7 | |
| | | | | | Z 14123 | 8 | |
| | | | | | H 14240 | 4.1 | Do. |
| | | | | | E 14236 | 4.3 | |
| 9 July..... | 107 | 1263.01 | 1268.46 | 1393.44 | F 14225 | 4.5 | |
| | | | | | G 14233 | 4.7 | |
| | | | | | Z 14152 | 0 | |
| 10 July..... | 108 | 217.35 | 217.33 | 0 | | | |
| | | | | | H 15019 | 4.1 | Do. |
| | | | | | E 15020 | 4.3 | |
| 10 July..... | 109 | 1306.60 | 1312.52 | 1455.37 | F .... | 4.5 | |
| | | | | | G .... | 4.7 | |
| | | | | | Z 14903 | 8 | |
| 12 July..... | 110 | 217.36 | 217.34 | 0 | .... | | |
| | | | | | H 14978 | 4.1 | Do. |
| | | | | | E 14980 | 4.3 | |
| 12 July..... | 111 | 1305.53 | 1311.35 | 1453.52 | F .... | 4.5 | |
| | | | | | G .... | 4.7 | |
| | | | | | Z 14867 | 8 | |
| | | | | | H 14980 | 4.1 | Do. |
| | | | | | E 14960 | 4.3 | |
| 12 July..... | 112 | 1305.46 | 1311.28 | 1453.31 | F 14947 | 4.5 | |
| | | | | | G .... | 4.7 | |
| | | | | | Z 14872 | 8 | |
| 13 July..... | 113 | 217.40 | 217.38 | 0 | .... | | |
| 10 Sept..... | 114 | 217.38 | 217.36 | 0 | .... | | |
| | | | | | H .... | 4.1 | *a* (1), *c* (2.3) |
| | | | | | E 15389 | 4.3 | *e* (6.7), *f* (7.3) |
| 11 Sept..... | 115 | 1328.68 | 1334.79 | 1484.70 | F 15374 | 4.5 | |
| | | | | | G .... | 4.7 | |
| | | | | | A 15357 | 8 | |
| | | | | | H .... | 4.1 | Do. |
| | | | | | E 15411 | 4.3 | |
| 11 Sept..... | 116 | 1332.18 | 1338.32 | 1489.60 | F 15417 | 4.5 | |
| | | | | | G 15418 | 4.7 | |
| | | | | | A 15421 | 8 | |
| 13 Sept..... | 117 | 217.62 | 217.60 | 0 | .... | | |
| | | | | | H .... | 4.1 | *a* (1), *c* (2.3) |
| | | | | | E 15391 | 4.3 | *e* (6.7) *f* (7.3) |
| 15 Sept..... | 118 | 1329.92 | 1336.03 | 1487.36 | F 15389 | 4.5 | |
| | | | | | G 15399 | 4.7 | |
| | | | | | A 15382 | 8 | |
| 16 Sept..... | 119 | 217.51 | 217.49 | 0 | .... | | |

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TABLE XIII.—OBSERVED GAS-THERMOMETER DATA—Continued.

Gas Filling No. 4—Continued.

| Date | No. | $p'$ (or $p_0'$) | $p$ (or $p_0$) | $t$ | Standard elements. | Position. | Other elements and positions. |
|---|---|---|---|---|---|---|---|
| | | | | | H .... | 4.1 | $a$ (1), $c$ (2.3) |
| 1909 | | | | | E 15386 | 4.3 | $e$ (6.7), $f$ (7.3) |
| 17 Sept. | 120 | 1329.68 | 1335.78 | 1486.95 | F 15376 | 4.5 | |
| | | | | | G 15368 | 4.7 | |
| | | | | | A 15379 | 8 | |
| | | | | | H .... | 4.1 | Do. |
| | | | | | E 15397 | 4.3 | |
| 17 Sept. | 121 | 1331.40 | 1337.51 | 1489.34 | F 15396 | 4.5 | |
| | | | | | G 15389 | 4.7 | |
| | | | | | A 15412 | 8 | |
| 18 Sept. | 122 | 217.52 | 217.50 | 0 | .... | | |
| | | | | | H .... | 4.1 | Do. |
| | | | | | E 14991 | 4.3 | |
| 21 Sept. | 123 | 1306.75 | 1312.72 | 1454.83 | F 14996 | 4.5 | |
| | | | | | G 14957 | 4.7 | |
| | | | | | A 14982 | 8 | |
| | | | | | H .... | 4.1 | Do. |
| | | | | | E 14979 | 4.3 | |
| 21 Sept. | 124 | 1307.28 | 1313.25 | 1455.60 | F 14984 | 4.5 | |
| | | | | | G 14952 | 4.7 | |
| | | | | | A 14996 | 8 | |
| 22 Sept. | 125 | 217.45 | 217.43 | 0 | .... | | |
| | | | | | H 10618 | 4.1 | $a$ (1.5), J (2.4) |
| | | | | | E 10626 | 4.3 | $c$ (6.2), $e$ (7.2) |
| 27 Nov[1]. | 126 | 1045.80 | 1049.49 | 1090.59 | F 10622 | 4.5 | |
| | | | | | G 10616 | 4.7 | |
| | | | | | C 10567 | 8 | |
| 29 Nov. | 127 | 217.28 | 217.26 | 0 | .... | | |
| | | | | | H 12002 | 4.1 | Do. |
| | | | | | E 12006 | 4.3 | |
| 9 Dec. | 128 | 1129.52 | 1133.91 | 1206.63 | F 12003 | 4.5 | |
| | | | | | G 12010 | 4.7 | |
| | | | | | C 11914 | 8 | |
| | | | | | H 13106 | 4.1 | Do. |
| | | | | | E 13112 | 4.3 | |
| 9 Dec. | 129 | 1194.81 | 1199.74 | 1298.01 | F 13107 | 4.5 | |
| | | | | | G 13115 | 4.7 | |
| | | | | | C 13007 | 8 | |
| | | | | | H 14246 | 4.1 | Do. |
| | | | | | E 14250 | 4.3 | |
| 9 Dec. | 130 | 1261.16 | 1266.68 | 1391.45 | F 14248 | 4.5 | |
| | | | | | G 14256 | 4.7 | |
| | | | | | C 14146 | 8 | |
| 10 Dec. | 131 | 217.30 | 217.28 | 0 | .... | | |
| | | | | | H 11940 | 4.1 | $a$ (1), J (2.3), |
| | | | | | E 11946 | 4.3 | $c$ (6.2), $e$ (7.1) |
| 20 Dec. | 132 | 1125.92 | 1130.29 | 1201.50 | F 11951 | 4.5 | |
| | | | | | G 11949 | 4.7 | |
| | | | | | C 11887 | 8 | |
| | | | | | H 14950 | 4.1 | Do. |
| | | | | | E 14958 | 4.3 | |
| 20 Dec. | 133 | 1302.40 | 1308.33 | 1450.03 | F 14962 | 4.5 | |
| | | | | | G 14955 | 4.7 | |
| | | | | | C 14882 | 8 | |
| | | | | | H 16156 | 4.1 | Do. |
| | | | | | E 16160 | 4.3 | |
| 20 Dec. | 134 | 1372.16 | 1378.78 | 1550.15 | F 16170 | 4.5 | |
| | | | | | G 16148 | 4.7 | |
| | | | | | C 16075 | 8 | |
| 21 Dec. | 135 | 217.29 | 217.27 | 0 | .... | | |

[1] Outside-wound furnace. See p. 56 and Fig. 10.

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## 14. THE TRANSFER TO THE FIXED POINTS.

After the thermo-elements are removed from the bulb, their E. M. F. at the fixed points must be determined by immersing them in melting or freezing metals or salts. The instrumental corrections to the readings so obtained were the same as in the case of the gas-thermometer readings. The error due to contamination was also present above 1100°, just as in the gas-thermometer furnace, and was a very disturbing factor in determining the melting-points of nickel, cobalt, and palladium. Its source, however, was not usually iridium vapor from the furnace or rhodium from the wire of the element, but was either vapor of the melting metal itself, or (when a hydrogen atmosphere was used) the products of reduction of silica. In the presence of hydrogen, silica rapidly deteriorates platinum wire by reduction and alloying, as has been shown in this laboratory by Shepherd,[1] and elsewhere by several observers. The contamination can be partly prevented by the use of a glazed procelain tube surrounding the thermo-element, instead of an unglazed magnesia tube; but an additional uncertainty is thereby introduced through the contamination of the melting metal by the melted glaze on the porcelain. For this reason nickel and cobalt did not prove to be as satisfactory fixed points as had been hoped, since it was necessary to melt them in an atmosphere of hydrogen. Palladium, however, can be melted in the open air and serious contamination by silicon thus be avoided, although the palladium itself gradually contaminates the wire.

Above 1100° it was found better to make direct comparisons of all the elements with one or two whose fixed points had been determined, rather than to contaminate them all by a direct determination. For making these comparisons, the plan first used was to bring a crucible of molten silver to a constant temperature and insert the elements (protected by a glazed Marquardt porcelain tube) successively into the silver bath. There is an uncertainty, however, in these measurements, of 2 to 3 microvolts caused by small differences of temperature within the tube and the slight cooling produced by introducing cold wires into the furnace. A better method is to join together the two platinum wires and the two alloy wires of the elements to be compared, and determine the small E. M. F.'s of each pair at several temperatures, from which the difference between the elements at those temperatures can be obtained by algebraic addition. This method offers a great advantage in that the temperature need be only approximately constant and approximately known, since the differences in most cases amount to only a few microvolts. By this method the comparison can be very quickly made at 1500° in the blast-lamp flame, which, with a little care, can be made to give a temperature constant to 20°.

All the metal melting-points here described, except that of palladium, were made in an upright cylindrical furnace through which passed a glazed porcelain tube which could be tightly closed above and below and therefore permitted the atmosphere about the melting metal to be perfectly controlled. An effort was first made to accomplish this by placing the entire furnace inside a gas-tight bomb in which the atmosphere could be similarly varied, but the persistent retention of gases by the various clay insulating

[1] Am. Jour. Sci. (4), 28, p. 300, 1909.

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materials used about the furnace made this method slow, cumbersome, and very uncertain in its results. The only success which these bomb furnaces attained was to permit melting-points to be measured in an approximate vacuum (about 1 mm. pressure). But it has since been found so much simpler to operate with a neutral or reducing atmosphere in the closed tube passing through the heated zone that the vacuum furnace has not been used for this work.

The chief disadvantage in the use of a tube of this kind is its effect upon the temperature gradient along the furnace axis. More heat is diverted toward the ends of the furnace and the central constant-temperature zone becomes shorter. It offers no difficulty except that greater care must be taken in locating the crucible within the constant-temperature region.

The qualities desired in fixed thermometric points for establishing and reproducing a scale are:

(1) Exact reproducibility of the temperature in repeated determinations with the same charge of material and with a different charge independently obtained. This means that the metal or salt must be obtainable either perfectly pure or with a constant amount and kind of impurity.

(2) Independence of particular experimental arrangements. The melting-point of a metal, for instance, must be sharp and definite enough so that with different kinds of furnaces *and different rates of heating* the same temperature will be obtained.

(3) Convenience and safety of manipulation. A melting-point which can only be obtained by the use of elaborate experimental arrangements is undesirable, even though it be reproducible and sharp. Furthermore, the substance must not injure the instrument to be calibrated.

1. *Reproducibilty.*—No extensive experiments have been made in the present work to test a large number of samples of different origin. It appeared sufficient to assure ourselves that all of the metals here used are obtainable in such degree of purity, or with such a constant amount of impurity, that the variations in their melting-points are well within the limits of error in the scale itself. Waidner and Burgess[1] have recently made comparisons of various samples of pure zinc, antimony, and copper, and have found no differences exceeding 0.3°.[2] Our experience has been the same. All of the metals in the present investigation are readily obtainable from the ordinary sources of supply. They have been carefully analyzed in this laboratory by Dr. E. T. Allen, and the results are given on page 85.

2. *Independence of Experimental Conditions.*—A number of experiments were made to test the effect of different experimental arrangements on the points. Two different furnaces were tried, one 65 mm. inside diameter and 150 mm. long, the other 55 mm. inside diameter and 230 mm. long. The region of constant temperature in the second furnace was longer than in the first and accordingly there was a larger range in which the crucible could be moved about without affecting the temperature. This furnace was used for all work after March 6, 1909. The ultimate test was always the agreement between the melting and freezing points. Any serious disagreement of these two in metals shows that some influence is entering from without.

[1] Phys. Rev., 27, 467–469, 1909. Bull. Bur. Stds., 6, 149–230, 1909.
[2] In the case of antimony, this statement applies only to Kahlbaum's metal.

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The results of the study were briefly as follows: (1) The best dimensions for a charge of metal are about 25 mm. diameter by 45 mm. deep. (2) The thermo-element tube should be about 5 mm. above the bottom of the crucible. (3) There is a region within the furnace in which the melting and freezing points agree and are independent of the rate of heating or (within limits) of the depth of immersion of the thermo-element; it is necessary to find this position of the crucible by trial. With this position once determined, the temperature of the zinc, antimony, silver, gold, and copper points can be relied upon within 0.2°. With large charges and facilities for stirring the metal, Waidner and Burgess have found the zinc point to be reproducible in a given furnace, with a given sample, within less than 0.1°.

White[1] showed that the temperatures of the two silicate points used for for the present scale are reproducible within 1.0° independently of the dimensions of the furnace or the rate of heating. For a mineral melting-point the charge should be small (about 3 grams), the heat should flow into the thermal junction from the side and not from the ends, and a position in the furnace should be found in which the melting-point, determined by a bare thermo-element, *does not vary with the rate of heating.*

The possibility has been several times suggested that the temperature of the thermo-element inside of the tube might possibly be lower by a small constant amount than the metal outside of the tube, and that this error might not be brought to light by such experiments as have been described. Several melting and freezing points of copper were therefore determined by inclosing the entire thermo-element wire in a thin capillary of silica glass which was slipped over the wire, bent double, and melted down upon the wire at the junction by heating in the oxy-hydrogen flame. This was dipped directly into the molten copper to within 5 mm. of the bottom, so that there was practically no possibility that the temperature of the junction could be lowered by radiation or conduction upward. The melting-point on element *D* obtained in this way was 10,473 microvolts as compared with 10,473 microvolts in the closed glazed tube. There appears to be no error from this cause.

3. *Convenience and Safety of Manipulation.*—Zinc and gold are the most convenient of manipulation, as they require no special atmosphere and the temperatures are easily reached. Antimony, silver, and copper require an atmosphere of carbon monoxide and are somewhat less convenient. More care needs to be taken with copper than with silver and antimony because of the considerable effect of a very small amount of oxide. Antimony, silver, gold, and copper were all melted in carbon monoxide, made by dropping formic acid into warm sulphuric acid, and purified by passage through sodium hydroxide, lead nitrate, and sulphuric acid. The lead nitrate was introduced to make certain that no trace of hydrogen sulphide, which might be formed if the acid became too dilute or too warm, could pass into the metal.

The two silicates (diopside and anorthite) and palladium were melted in air. The silicate points are very convenient to arrange and manipulate, provided the furnace is well insulated so that the temperature can be reached

[1] Diopside and its relations to calcium and magnesium metasilicates, Am. Journ. Sci. (4), 27, p. 4, 1909.

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without difficulty. Palladium strains the platinum resistance furnace near to its limit of endurance on account of the high temperature, but has the great convenience of not requiring a reducing atmosphere. Special pains need to be taken, however, in this case, to protect the thermo-element from contamination.

Nickel and cobalt were melted in an atmosphere of hydrogen which was made by electrolysis in a large glass and earthenware generator, and purified by passage through potassium pyrogallate and sulphuric acid. Just before the thermo-element was introduced, the hydrogen was displaced by pure nitrogen drawn from a steel tank in which it was stored under pressure. The supply contained a trace of hydrogen and was, therefore, purified by passing over hot copper oxide and through calcium chloride and sulphuric acid. The extreme lightness of hydrogen compared with the outside air (especially when it is heated to 1450°) makes necessary special precautions in order to keep out any trace of air. Furthermore, hydrogen always caused contamination in the thermo-element, which was not prevented even when the hydrogen was replaced for a short time during the melting by pure nitrogen. Nickel and cobalt are, therefore, not recommended for frequent use in the calibration of thermo-elements, if the two points, diopside and palladium (or diopside and anorthite), give a sufficient calibration for the purpose in hand.

The apparatus used for the melting-points of nickel and cobalt is shown in section in Fig. 13. The top of the large porcelain tube (Marquardt, glazed outside only) was closed by a sliding cup of brass in which the thermo-element tube and two others for introducing hydrogen were fastened by heating the cup and pouring in molten solder. The porcelain tube extended far enough out of the furnace to keep the brass cup cool. A groove near the base of the cup carried a piece of asbestos cord which made a gas-tight joint with the porcelain tube and permitted the whole to be raised and lowered without moving the crucible or opening the top of the tube. Two diaframs of Marquardt porcelain above the crucible also prevented any considerable radiation upward to the brass cup.

In zinc, antimony, silver, gold, and copper, the thermo-element was protected by a glazed Marquardt tube of 5 mm. inside and 8 mm. outside diameter. In the case of antimony, the tube was further protected by a thin tube of graphite which fitted into the cover of the crucible. With diopside and anorthite, some contamination from iridium in the furnace may take place, but can be largely prevented by surrounding the supporting tube with pure platinum. Here the thermo-element dips directly into the molten silicate. A glazed Marquardt tube can not be used with the silicates, for the glaze flows readily at these temperatures and may make its way into the charge. With nickel and cobalt, glazed Marquardt tubes and also pure magnesia tubes of the same size were used, but neither protects the element perfectly from contamination. In palladium only the pure magnesia tubes were used.

Zinc, antimony, silver, gold, and copper were melted in graphite crucibles 27 mm. in diameter and 80 mm. deep inside, and 37 mm. in diameter and 100 mm. high outside. The charge of metal was from 45 mm. to 55 mm. deep. Diopside and anorthite were melted in small platinum crucibles 10

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mm. in diameter and 18 mm. deep, suspended by platinum sleeves from the open end of unglazed Marquardt tubes, as described and illustrated in the paper already referred to.[1]

Nickel was melted in an unglazed Marquardt porcelain crucible, lined with a paste consisting of about 90 per cent $Al_2O_3$ and 10 per cent MgO; and also in a Berlin "pure magnesia" crucible. The charge was about

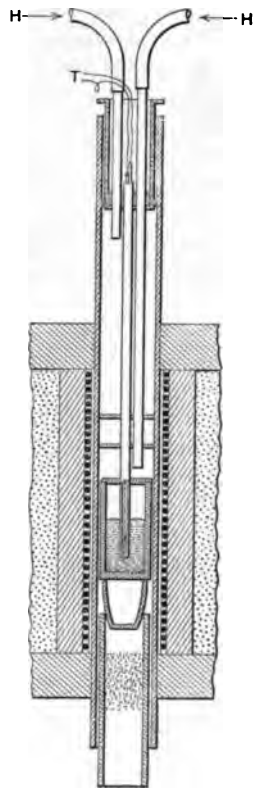


FIG. 13. The furnace in which the cobalt and nickel melting-points were made, showing the position of the metal with respect to the coil, the thermo-element (T) and the arrangement (H) for maintaining a hydrogen or nitrogen atmosphere.

25 mm. in diameter and 30 mm. deep. Cobalt could not be melted in the alumina-lined crucible, as the metal penetrated through the lining and attacked the porcelain. It was, therefore, melted in a "pure magnesia" crucible made by the Königliche Porzellan Manufaktur. The material of these crucibles probably contains a small percentage of silica. Palladium was melted in a crucible made in this laboratory from a specially pure magnesia made by Baker and Adamson. The magnesia was first shrunk by heating to a temperature higher than that at which the crucible was to

[1] W. P. White, Am. Jour. Sci. (4), **28**, p. 477, 1909.

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be used, and was then made into a paste with water and a little magnesium chloride, spun into form, and baked.

In choosing the materials for such determinations, two not altogether concordant standpoints must be recognized: (1) The materials used must be of absolutely known composition and of high purity in order to give the melting-point determinations a positive significance; (2) the same materials in the same purity must be easily obtainable by other investigators in order to enable the results to be conveniently utilized by others if desired.

Metal melting-points were given the preference over pure salts which have been repeatedly suggested for this purpose, (1) on account of the greater sharpness of the melting-point, (2) on account of their general availability for such determinations, and (3) because of the now very generally established custom of comparing the results of different observers through the medium of these standard melting-points. The metals used in this investigation were from various sources, which will be specified below. Each has been very carefully described and analyzed by Dr. E. T. Allen of this laboratory, whose report is printed in full on page 85 and following. We prepared none of the metals ourselves. Those which were used were purchased from firms who may fairly be expected to supply the same nominal quality to any other investigator who may care to use them, but it must be emphasized in this connection that metals furnished under the same description by the same dealer at different times have not always proved of uniform purity and probably can not at present be expected to be so. The variations in the thermal behavior of the different samples is not great, never amounting to more than 1° in our experience; but we are of course unable to offer any guarantee that the same metals obtained in future will remain within this limit, nor is the dealer's guarantee at present a sufficient protection.

As the situation now stands, the errors in the gas-thermometer measurements are of the same order as the differences between the melting-points of different samples of a given metal obtained at different times from the same dealer and of the same (nominal) purity. This may serve to emphasize more than ever before the desirability of a provision, preferably by some national bureau of standards, for standard metals, the uniform purity of which can be absolutely depended upon, and in terms of which such constants can be expressed. In the absence of such a provision, it is difficult to see just how to make the gas scale conveniently available for general use in its full accuracy. This is furthermore a matter of considerable importance in view of the extended extrapolation to which the gas scale is frequently subjected by the use of thermo-elements or otherwise. Supposing the metal melting-points to be capable of reproducing the temperature curve correctly within 1° at the copper point (1082.6°), an extrapolation to 1500° may easily remain uncertain by as much as 10° in the hands of different individuals using the same function for the extrapolation.

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## 15. THE METALS USED.

(By E. T. Allen.)

The object of these analyses was primarily, of course, to decide whether the metals should be used or rejected for the temperature scale, and those selected were examined very carefully, so that in the future, when more is known about the specific lowering which the various impurities produce on the melting-point, corrections may be made if desirable. The methods used in these analyses are given in so far as it has been deemed necessary. Details, especially in those cases where well-known procedure is followed, have been purposely omitted.

The accuracy of the determinations can not be stated absolutely. There is of course the possibility of increased solubility of difficultly soluble compounds in the comparatively concentrated solutions of the metals from which the impurities have to be precipitated, viz, 5 to 6 g. in 250 cc. volume. Also, when it is necessary to separate the bulk of the metal by precipitation from the impurities, as it sometimes is, one can not be sure that the impurity sought is not occluded by the precipitates. In most cases, the latter source of error is probably the more serious. Only methods worked out synthetically with materials laboriously prepared could decide these questions.[1] Large quantities of metal, 25 to 100 g., were generally taken for analysis, and since the impurities were weighed to the tenth of a milligram, the results are generally stated to the ten-thousandth of 1 per cent. This does not mean that the results are considered accurate to this figure. The variation in successive determinations comes in the thousandths, so that the fourth decimal place may have about as much value as the second in an ordinary analysis. Great pains have been taken to purify precipitates, often by many precipitations, so that in all cases the figures given may be regarded as minima. In all cases, too, I have endeavored to avoid missing anything, by repeating every process, rejecting no precipitate or solution until it was decided that nothing more was to be gotten from it. In any reasonable case of suspicion, blank determinations were made with the reagents.[2]

### CADMIUM.

Eimer and Amend's "Cadmium metal sticks" purchased in 1904 was used. Inasmuch as the cadmium melting-point was used for the purpose of extrapolation only (p. 116) and but a single gas-thermometer measurement made upon it, less care was necessary in the analysis of it than in the more important metals which follow. The details are accordingly omitted. Its analysis is given on page 86.

[1] The data on this question which are known to me are quite meager. An interesting instance is given by Mylius and Fromm (Z. anorg. Chem. 9, 144–147, 1895), using a specimen of zinc in which they could detect no impurities. Additions of only 0.1 mg. of lead, cadmium, or mercury to a solution of 40 grams of this zinc could be detected qualitatively.

[2] After considerable experience in the examination of these "pure" metals the writer has reached the conclusion that a 10-gram portion, in the great majority of cases, will give as satisfactory results as a larger portion and with far less labor.

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ANALYSIS OF CADMIUM.

| | |
|---|---|
| As | None |
| Cu | Trace |
| Pb | .0860 |
| Zn | Trace |
| Fe | .0025 |
| Co | None |
| Ni | None |
| S | .0005 |
| Total impurities | .0890 per cent. |

## ZINC.

This metal was obtained in the form of sticks from the firm of Eimer and Amend. The method of Mylius and Fromm was followed for the principal impurities.[1] 100 grams were dissolved in nitric acid. The solution was then diluted and ammonia was added until the zinc at first precipitated was entirely redissolved. Then enough hydrogen sulphide was added to throw down all the impurities of the hydrogen sulphide and ammonium sulphide groups together with considerable zinc. The precipitate was filtered off and further separations were made as usual.

The platinum metals and gold were not looked for, as it was thought quite improbable they would be present, but arsenic and antimony were sought for by Günther's method.[2] This consists in the volatilization of the hydrides of these metals which are separated from the hydrogen, which forms at the same time, by passing the gas through silver-nitrate solution. A special form of apparatus was used which consists of a 1-liter round-bottom flask with long neck 35 mm. wide at the top. This is closed by a glass stopper in which are sealed a small glass tube passing to the bottom of the flask and serving to fill the flask with hydrogen and to replace the gases formed in the experiment; a dropping funnel through which the acid used to dissolve the zinc is introduced, and lastly, an upright outlet tube surrounded by a small condenser. The outlet was connected with a wash bottle containing a solution of silver nitrate. As pure zinc dissolves with difficulty in dilute hydrochloric acid, the metal was reduced to the form of shavings by the aid of a lathe. Fifty grams of these shavings were introduced into the flask, the air in which was at once replaced by hydrogen. Dilute hydrochloric acid was then let in through the dropping funnel. The solution was facilitated by warming. At the end of the operation, the gas in the flask was driven out by pure hydrogen. The silver-nitrate solution, which contained a black precipitate, was then filtered. The antimony in the precipitate was determined by dissolving it in nitric acid with the addition of a little tartaric acid, precipitating the silver with hydrochloric acid, evaporating the filtrate to dryness on the steam bath, and precipitating by hydrogen sulphide. The precipitate was dissolved in a few drops of ammonium sulphide, the solution filtered into a small tared porcelain capsule, evaporated, decomposed by nitric acid, and weighed as $Sb_2O_4$. After separating the silver from the first filtrate which contained the arsenic, it was evaporated to dryness, reduced with sulphurous acid, and precipitated by hydrogen sulphide. None was detected with certainty.

[1] Zeitschr. anorg. Chem., 9, 144, 1895.
[2] Lunge, Chem.-tech. Methoden (1905), ii, 322. Zeitschr. analyt. Chem., 20, 503–507, 1881.

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If this solution had been tested by Marsh's method, no doubt a trace would have been found, but as its quantity was of a different order of magnitude from the other impurities it was not thought worth while to make the test. Günther determines sulphur at the same time with arsenic and antimony, by interposing between the generator and the absorption cylinder which contains the silver nitrate another cylinder containing potassium-cadmium cyanide, which absorbs all the hydrogen sulphide and, according to him, retains no arsenic and antimony. Since a solution of this cadmium compound is always alkaline, it was thought safer to take a separate portion of zinc for the estimation of sulphur, silver nitrate being used as the absorption reagent. The small precipitate was examined for sulphur by dissolving in nitric acid and proceeding as usual. Found 0.4 mg. $BaSO_4$. Blank gave 0.3 mg. $BaSO_4$.

The zinc was tested for silicon in the same way as the copper. (See p. 92.)

ANALYSIS OF ZINC.

| | |
|---|---|
| As | Not found |
| Sb | .002 |
| Sn | Not looked for |
| Au | Not looked for |
| Pt | Not looked for |
| Ag | None |
| Bi | None |
| Pb | .051 |
| Cd | .004 |
| Ni | None |
| Co | None |
| Fe | .006 |
| Si | None |
| S | None |
| | .063 per cent. |

## ANTIMONY.

Twenty-five grams of metal were powdered in an agate mortar and treated with 35 per cent $HNO_3$ on the steam bath. As soon as the reaction was practically complete, the antimonic acid was extracted with hot dilute nitric acid, transferred to a filter, and washed with water. The filtrate and washings were then evaporated to dryness with hydrochloric acid, while the antimonic acid was digested repeatedly with yellow sodium sulphide till the soluble portion was dissolved. The residue, after a little washing, was dissolved in nitric acid, evaporated to dryness, freed from nitric by hydrochloric acid, and the chlorides united with the first extract. The whole was precipitated by hydrogen sulphide. The washed sulphides were then extracted with colorless ammonium sulphide. From this solution the sulphides were thrown down by acid, filtered, and washed. Then they were dissolved in hot dilute caustic potash. The solution was boiled with perhydrol for complete oxidation, and arsenic sought for by Fischer's method, viz, reducing by ferrous ammonium sulphate and distilling in a current of hydrochloric acid gas. No As.

A separate portion of 5 grams was taken for tin. McCay's method[1] was tried. $SnO_2$ = 1.3 mg. Sn = 1.0 mg. = 0.02 (?) per cent.

A separate portion of 25 grams was used for sulphur. The metal was oxidized by nitric acid as before, and the soluble portion separated and

[1] Private communication.

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evaporated. The residue was then heated with a small excess of sodium carbonate and filtered. The residue was also boiled out several times with sodium carbonate solution. The two solutions were then acidified with hydrochloric acid and treated with barium chloride. The portion soluble in nitric acid gave a slight precipitate, which was further purified, after the usual washing and drying, by fusion with sodium carbonate. The water extract containing the soluble sulphate was acidified and precipitated a second time. $BaSO_4$ = trace.

ANALYSIS OF ANTIMONY.

| | |
|---|---|
| As | None |
| Sn | 0.02 (?) |
| Ag | None |
| Pb | Trace (?) |
| Cu | 0.004 |
| Bi | None |
| Cd | None |
| Ni | None |
| Co | None |
| Mn | None |
| Zn | None |
| Fe | 0.007 |
| S | Trace (?) |
| | 0.031 per cent. |

## ALUMINUM.

Owing to the difficulty of handling this metal, small portions (10 grams) only were taken for analysis. Heavy metals, except arsenic and antimony, were sought for in the hydrochloric acid solution by ordinary methods. Only a trace of copper was found.

For phosphorus, arsenic, and sulphur, a separate portion was dissolved in caustic alkali in a special apparatus entirely of glass. The vessel was first filled with purified hydrogen and then the alkali was introduced and the gases evolved were passed through silver-nitrate solution. At the end, the gases remaining in the vessel were displaced by hydrogen. The precipitated silver was worked over for the different elements. No As or Sb. A separate portion was used for sulphur. $BaSO_4$ = 1.4 mg. S = 0.002 per cent.

To determine the silicon, 10 grams of metal were dissolved in a mixture of nitric and sulphuric acids, using a platinum dish. With hydrochloric acid alone nearly all the silicon is lost as hydride. The brown amorphous residue was filtered, washed, and fused with sodium carbonate. From the fusion silica was obtained in the usual way. $SiO_2$ = 41.4 mg. Si = 0.194 per cent. Repetitions gave 0.189 per cent and 0.190 per cent.

For the carbon, 10 grams of metal were dissolved in NaOH and filtered through glowed asbestos, washed first with water, then with dilute acid, finally with water, and dried at 105°. The asbestos and residue were then transferred to a combustion tube and burned in air free from $CO_2$. The gases were passed through standard $Ba(OH)_2$. A considerable precipitate was obtained, while a blank gave no trace. The excess of $Ba(OH)_2$ was then titrated with standard acid, using phenolphthalein as indicator. 5.05 mg. $CO_2$ found. C = 0.014 per cent. A duplicate in which the metal was dissolved in KOH gave 0.012 per cent.

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For the iron, 10 grams of metal were dissolved in hydrochloric acid, and to the solution was added tartaric acid free from iron. From this solution the iron was precipitated by colorless ammonium sulphide. The precipitate was finally changed to sulphate and determined volumetrically. Fe = 4.6 mg. Blank determination gave 0.3 mg. Fe = 0.043 per cent.

Calcium, sodium and potassium were sought for in the hydrochloric-acid solution, by precipitating with ammonia, washing the large precipitate, and testing the evaporated filtrate. No Ca. Some alkaline chloride was found, but a blank showed that it came from the ammonia, as there was only a difference of 1.6 mg. between the chloride of the blank and that in the determination. No Na or K.

ANALYSIS OF ALUMINUM.

| | |
|---|---|
| As | None |
| Sb | None |
| P | None |
| Cu | 0.003 |
| Fe | 0.043 |
| Si | 0.190 |
| C | 0.013 |
| S | 0.002 |
| Ca | None |
| Na | None |
| K | None |
| | 0.251 per cent. |

## SILVER.

This metal, as well as the gold, was prepared by Mr. Eckfeldt at the Philadelphia Mint. A block weighing about 100 grams was cut from a larger brick with a hard cold chisel and, after cleaning, transferred to a large casserole of Berlin porcelain and dissolved in a slight excess of nitric acid. During the operation the dish was covered with a watch-glass. A small black residue was now filtered off on the felt of a large porcelain Gooch crucible, then washed and dried. The asbestos of the felt was previously heated to redness. The residue was then laid in a porcelain boat which was slipped into a combustion tube containing copper oxide and heated in a current of oxygen. The outflowing gas was passed through a very dilute standard solution of barium hydroxide, 1 cc. = 0.97 mg. of $CO_2$, in which a decided white precipitate appeared at once. The excess of baryta was then titrated with standard acid. A blank determination *previously* made gave no precipitate in the baryta water. This determination is of no importance as regards the melting-point of the silver, since the metal had to be melted in graphite, but considering the source of the silver and its unusual degree of purity the determination may be of some interest. What remained of the residue after the carbon was burned was extracted with aqua regia. The solution was evaporated to dryness and taken up with hydrochloric acid, and the gold was precipitated by sulphur dioxide. The filtrate from gold gave a slight black precipitate with hydrogen sulphide. This precipitate weighed only 0.1 mg. after it had been glowed in a small porcelain crucible, but it remained black, dissolved in a few drops of aqua regia which left a yellow stain when evaporated, and gave a very strong rose color when dissolved in water and tested with a drop of potassium iodide—all character-

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istic of platinum. It was suspected that a trace of platinum might exist in the acid used to dissolve the silver, but a blank test on the same quantity of reagent proved the contrary. The silver solution was now diluted to several liters and precipitated with hydrochloric acid. The filtrate was evaporated in porcelain to a small volume and in this the remaining impurities were sought for by well-known methods. Only lead and iron and the merest trace of copper were found.

A blank determination was made for iron. Found in the silver+reagents 0.0013 per cent; in the reagents, 0.0002 per cent; leaving 0.0011 per cent in the silver.

For the estimation of sulphur, a separate portion of 38 grams was taken, the silver was removed in the same manner, and the filtrate evaporated to dryness in porcelain. The small residue was then evaporated again with hydrochloric acid to decompose nitrates. The final residue was dissolved in a small volume of water acidulated with hydrochloric acid, filtered to remove any silver chloride which might have escaped precipitation, and precipitated with barium chloride. Found 1.4 mg. $BaSO_4$, while the same quantity of reagents gave 0.4 mg. $BaSO_4$: S=0.0004 per cent.

ANALYSIS OF SILVER.

| | | | |
|---|---|---|---|
| As | None | Hg | None |
| Sb | None | Cd | None |
| Sn | None | Zn | None |
| Au | .0005 | Ni | None |
| Pt | .0001 | Co | None |
| Cu | Mere tr. | Fe | .0011 |
| Bi | None | S | .0004 |
| Pb | .0008 | C | .0003 |

0.0032 per cent.

## GOLD.

About 350 grams of "proof gold" were obtained from the Philadelphia Mint. It was prepared by Mr. Jacob Eckfeldt. A sample of gold prepared in a similar manner by Mr. Eckfeldt was used by Professor Mallet in his determination of the atomic weight of this metal. The method of purification is given in the Am. Chem. Jour., VII, 73, 1899. Professor Mallet found no systematic difference between this gold and two other samples, one of which was obtained from the Mint of England, and the other of which was prepared by himself. In view of these facts, it was evidently unnecessary to analyze the gold.

## COPPER.

The copper was of the form known as "copper drops cooled in hydrogen" and was obtained from Eimer and Amend of New York. Not all copper of this brand is equally pure. The sample analyzed was a portion of a 25-pound lot. The method followed in the analysis was essentially that of Hampe,[1] in which the copper is separated from the impurities by precipitation as cuprous thiocyanate. A 100-gram portion was placed in a large casserole of Berlin porcelain, dissolved in nitric and sulphuric acids, and

[1] Lunge, Chem.-tech. Methoden (1905), vol. II, 202. Chem. Ztg. 17, 1691–1692, 1893.

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the solution was then evaporated to drive off the excess of nitric acid. This troublesome operation can be greatly facilitated by the use of a crown burner, though, as dilution and evaporation have to be several times repeated, small losses are difficult to prevent. Duplicate determinations, however, proved that they were entirely negligible as regards the small percentage of impurities. The sulphate of copper was now dissolved in water and diluted. A little HCl was added and, after standing, the solution was filtered. The residue left on the filter was extracted with ammonia to remove silver chloride and the remaining part of it was treated with aqua regia. There was still left a little silica, from the porcelain dish in which the copper was dissolved. The solution obtained by aqua regia after the nitric acid was entirely driven out by hydrochloric acid was tested for gold by sulphur dioxide. There was no precipitate in the cold even after long standing, though evaporation caused the precipitation of about 0.5 mg. of black metal. This remained black on heating, dissolved only partially and with difficulty in aqua regia, and with sulphuric acid and ammonium nitrate gave a faint blue color. These tests indicate iridium, though there was too little to identify with certainty. The rest of the solution which had been tested for gold was precipitated by hydrogen sulphide and the precipitate was filtered, washed, and burned in a porcelain capsule. It formed a yellow chloride with aqua regia, gave a precipitate with ammonium chloride and a very strong test for platinum with potassium iodide. This platinum did not come from the acids used to dissolve the copper, since the same quantities were very carefully tested by hydrogen sulphide after nearly the whole portion had been driven off by heating in porcelain, and were found to contain not a trace.

The solution containing the copper was then warmed and saturated with sulphur dioxide. After standing, a further portion of silver was precipitated, filtered off, and washed. It was then dissolved in a little nitric acid, precipitated again as chloride, and added to the main portion of the silver chloride, which was dried at 130° and weighed.

The solution still containing the copper was diluted to about 8 liters, and from it all but a small portion of the copper was precipitated by a standard solution of potassium thiocyanate, 1 cc. of which was equivalent to about 50 mg. of copper. The thiocyanate was proved to be free from heavy metals by a test with hydrogen sulphide. The small amount of iron which it contained was separated before the solution was standardized, by the addition of a little ammonium alum followed by ammonia. The solution was allowed to stand and then filtered from iron and alumina. The precipitation of the copper was done very gradually with constant shaking to avoid carrying down the impurities, and after long standing was filtered. The filtrate was concentrated to a small volume in porcelain. A small additional precipitate which came down in this process was worked over with care to avoid any possible loss of impurities, especially lead, though no metal but copper was found in it. The filtrate was then examined as usual.

A word is needed in reference to the presence of zinc. This was found in every sample examined, in fact, it was generally the chief impurity. It was suggested that this zinc, or at least a part of it, might have come from the large flasks of Jena glass in which the acid solutions of the copper stood.

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To test this point, a sample of copper in which had been found 0.089 per cent of zinc was tested again. In this determination Jena glass was entirely discarded. The zinc found was 0.091 per cent. As these results agree within the limits of error, it is evident that Jena glass under these conditions will not contaminate solutions with zinc, at least in quantities of this order of magnitude. For the determination of silicon in the copper, 25 grams were placed in a platinum basin, dissolved in nitric and sulphuric acids, and evaporated over a crown burner to white fumes. The residue was dissolved and filtered. The filter was burned and the small residues tested for silica by hydrofluoric and sulphuric acids. Since it was feared that some silica might come from the watch glass used to cover the platinum dish during this operation, a blank was carried out with the reagents under the same conditions. Within the limits of error none was found.

For the estimation of sulphur the method of Lobry de Bruyn[2] was used, in which the copper is separated from the nitric acid solution by electrolysis. Twenty-five grams of metal was dissolved in 75 cc. nitric acid diluted with about an equal quantity of water, and then the excess of acid evaporated as far as possible on the steam bath. The electrolysis was done in a large platinum basin, which served as a cathode. The basin was covered with a glass plate pierced to admit a cylindrical platinum crucible which formed the anode. The current density was about 0.015 $\frac{\text{amp.}}{\text{sq. cm.}}$. After a time it was found necessary to pour off the solution from the precipitated copper and remove the free acid by another evaporation. A repetition of this operation is advisable. The filtrate from the copper is evaporated to dryness in porcelain and the small residue of nitrates decomposed by hydrochloric acid. The final residue is dissolved in acidulated water and precipitated by barium chloride.

Found in 25 grams copper ..... 4.2 mg. $BaSO_4$
Found in 75 cc. nitric acid ..... 0.6 mg. $BaSO_4$
3.6 mg. $BaSO_4$ = 0.002 per cent.

ANALYSIS OF COPPER.

| | | | |
|---|---|---|---|
| As | None | Bi | None |
| Sb | None | Pb | None |
| Sn | None | Cd | None |
| Se | None | Zn | .0007 |
| Te | None | Ni | None |
| Au | None | Co | None |
| Pt metals | .0011 | Fe | .0038 |
| Ag (separate determinations) | .0007, .0005 | Si | None |
| | | S | .0020 |

0.0083 per cent.

NICKEL.

Two 50-gram portions of Kahlbaum's electrolytic nickel were dissolved separately in measured quantities of nitric acid and then carried to white fumes with excess of sulphuric acid. Both portions were then dissolved in water and filtered. There was a small dark residue which was washed thoroughly and extracted with aqua regia, leaving a little silica from the dish. The yellow chloride obtained was freed from nitric acid, saturated with $SO_2$, and left to stand. No gold. Changed to chloride again and tested with caustic soda and $H_2O_2$. Still no gold. Acidified and repre-

[2] R. des trav. chim. de Pays-Bas, 10, 125, 1891.

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cipitated with $NH_4Cl$, a characteristic yellow precipitate was obtained. Confirmed by dissolving the chlor-platinate in hot water and precipitating by hydrogen. Pt = 2.3 mg. = 0.0023 per cent. The main solution was then precipitated by $H_2S$ (volume, 2 liters). The small black precipitate obtained was worked over for gold and platinum together with the above.

Other heavy metals were tested for in the ordinary way. 0.2 mg. $PbSO_4$ = about 0.1 mg. Pb. Cu = 52.3 mg. = 0.0523 per cent.

*Ammonium Sulphide Group.*—The voluminous solution was now freed from hydrogen sulphide by evaporation, some ammonium persulphate was added, and a stream of air passed through the solution for some time. No manganese.

$Fe_2O_3$ = 6.1 mg., after repeated precipitation. Fe = 4.2 mg.

Repeated efforts were made to separate zinc with $H_2S$ on the principle of the lower solubility of ZnS in dilute acids, but without satisfaction. First I tried to precipitate a small fraction of the nickel, hoping to get all the zinc with it. The volume of the solution was about 5 liters. But unless so much acid was added that strong doubts were entertained of recovering any zinc that might be present, the fraction of the nickel precipitate was far too great. Again, all the nickel was precipitated and the precipitate was digested with cold 10 per cent solution of hydrochloric acid. Here one had to fear either the failure to remove the zinc or the removal of too much nickel to handle without so many precipitations that a small quantity of zinc would probably be lost. It is doubtful whether we have any method which will give very small amounts of zinc in metallic nickel.

The whole solution was now tested for cobalt as follows: It was freed from $H_2S$ by evaporation, acidulated with HCl, and precipitated by $\alpha$-nitroso-$\beta$-naphthol in 50 per cent acetic acid. This was added in several portions. After long standing the precipitate was collected and washed. The voluminous precipitate was very cautiously burned in a capacious porcelain crucible. Much tar was formed. The residual oxide was dissolved in nitric acid and the cobalt was separated from nickel by $KNO_2$ in the usual way. The potassium cobalto-nitrite was finally decomposed by sulphuric acid and precipitated electrolytically from ammoniacal solution.

Co = 101.4 mg. + 4.9 mg. recovered from filtrate and weighed as sulphate. Total = 0.1063 per cent.

Fe and Co were also determined in a separate 10 g. portion of metal. $Fe_2O_3$ = 0.7 mg. Fe = 0.49 mg. = 0.0049 per cent. Co = 10.3 mg. = 0.1030 per cent.

A separate 10-gram portion was taken for sulphur. It was dissolved in nitric acid and evaporated on the water bath. This solution was diluted and precipitated with a slight excess of sodium carbonate. The filtrate was just acidulated, evaporated, and treated with barium chloride. No precipitate.

ANALYSIS OF NICKEL.

| | | | |
|---|---|---|---|
| Au | None | Bi | None |
| Pt | .0023 | Cd | None |
| As | None | Zn | None found |
| Sb | None | Co | .1063 |
| Sn | None | Mn | None |
| Pb | .0001 | Fe | .0042 |
| Cu | .0523 | S | None |

0.165 per cent.

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## COBALT.

Two 25-gram portions of Kahlbaum's metallic cobalt in the form of powder were dissolved in 150 cc. water + 35 cc. concentrated $H_2SO_4$. The analysis was quite similar to that of the nickel.

In the $H_2S$ group were found: Cu = 8.9 mg. = 0.0178 per cent. $PbSO_4$ = 12.9 mg. Pb = 0.0176 per cent.

In the $(NH_4)_2S$ group manganese was tested for as in the nickel. None was found. $Fe_2O_3$ = 0.9 mg. Fe = 0.0006 per cent.

As the tests for Ni and Zn were unsatisfactory, another portion of 25 grams was dissolved in dilute sulphuric acid and precipitated by $H_2S$.

The filtrate from the sulphides was filtered and freed from excess of $H_2S$ by evaporation. Then it was diluted to 1 liter and divided into two portions. Both were neutralized by sodium carbonate. In the one, manganese was sought for by ammonium persulphate. In the other nickel was looked for. A little ammonia was added and then an alcoholic solution of dimethylglyoxime. A precipitate containing much cobalt was obtained. This was worked over for nickel but none was found. For sulphur the method used in the analysis of nickel was followed. $BaSO_4$ = 14.4 mg., blank = 5.1 mg., difference = 9.3 mg., S = 0.013 per cent.

ANALYSIS OF COBALT.

| | | | |
|---|---|---|---|
| Ag | None | Bi | None |
| Au | None | Cd | None |
| Pt | None | Zn | None |
| As | None | Ni | None |
| Sb | None | Fe | .0006 |
| Sn | None | Mn | None |
| Pb | .0176 | S | .013 |
| Cu | .0178 | | |

0.049 per cent.

## HERAEUS'S PALLADIUM.

The palladium was naturally suspected to contain other metals of the platinum group. It is well known that the separation of these metals is a problem of unusual difficulty. The plan here was therefore to precipitate most of the palladium from solution as one of its characteristic compounds and, while the filtrate was reserved for impurities, to redissolve and again precipitate the metal as another characteristic compound. In this way it was hoped that those impurities retained by the first precipitate would not be occluded by the second The sheet metal was first cut into shavings on a milling machine especially cleaned for the purpose. Then the shavings were boiled a short time with dilute hydrochloric acid to remove any iron from the surface, and then washed and dried. After an unsuccessful endeavor to dissolve the palladium in nitric acid (insoluble brown hydroxide (?) always formed), it was dissolved in aqua regia and rid of nitric acid by successive evaporations with excess of hydrochloric acid. It was then dissolved in dilute hydrochloric acid and diluted further to about one liter. Ammonia was added in excess.[1] A precipitate came down and redissolved on warming, all but a little ferric hydroxide, which was filtered off. The filtrate was then evaporated again to about 250 cc., and then diluted and precipitated

[1] E. F. Smith and H. F. Keller, Amer. Chem. Jour., 14, 423, 1892.

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with stirring, by dilute hydrochloric acid. The voluminous precipitate of $PdCl_2 . 2NH_3$ was now filtered and washed on a Büchner porcelain funnel, using suction. The filtrate we will call "solution A." The precipitate was then dried and ignited in a large porcelain crucible. The resulting metal was dissolved in aqua regia and freed of nitric acid. This solution was diluted and precipitated by potassium iodide, and the filtrate ("solution B") removed as above.

From solutions A and B, separately, the platinum metals were first removed by long boiling with ammonium formate. The metal—1 to 2 grams in weight, mostly palladium—was filtered and the filtrate and washings were examined further for other heavy metals by the usual methods.

*Separation of the Palladium from the Platinum Metals.*—Considering now the ammonium-formate precipitate, Erdmann and Makowka[1] have obtained satisfactory separations of palladium from platinum and iridium by treating the solution of the mixed chlorides with acetylene. Palladium comes down as acetylide and the other metals are unprecipitated. I found also that rhodium solutions even on heating were not precipitated by acetylene. As for osmium, the ease with which it oxidizes and the high volatility of its oxide makes its elimination, in the process of preparing the palladium, fairly certain. Ruthenium, the rarest element among the platinum metals, need hardly be looked for; still it was sought for in the iridium found. The acetylene method was used, for lack of a safer one, though very tedious. In solutions at all concentrated, I find the palladium ceases to precipitate long before it is entirely removed from solution. Perhaps this is due to the accumulation of acid liberated in the process. At least, when the solution is separated from the acetylide, evaporated and diluted again, acetylene brings down another portion. After five or six operations, a residual solution was obtained on which acetylene had no further action. The acetylide was now carefully ignited with a little ammonium nitrate, the metal redissolved, and the whole process repeated. The residual solution was then added to the first and from it $NH_4Cl$ brought down platinum.

In the chlor-platinate no iridium was found. It was ignited, and the metal was entirely soluble in a few drops of aqua regia. It was again precipitated with $NH_4Cl$ and finally weighed as platinum. Pt = 1.6 mg. = 0.007 per cent. No rhodium was found in the filtrate. In the attempt to dissolve in aqua regia the several portions of metal formed by igniting the acetylide, tiny insoluble residues accumulated. These were fused with $KHSO_4$, which, as is well known, dissolves palladium and rhodium, but not iridium or platinum if the temperature is kept low. The soluble portion was dissolved in water and precipitated with ammonium formate. It turned out to be palladium, since it was precipitated by potassium iodide and no trace of rhodium was found.

The portion insoluble in $KHSO_4$ was freed from silica (which came from the dish) by HCl + HF, and was then ignited and weighed. Ir + Ru (?) = 1.9 mg. = 0.008 per cent. When fused with $K_2CO_3 + KNO_3$, some blue insoluble $IrO_3$ was formed, but the fusion showed no yellow color, and in view of the minute quantity of material, it was not thought worth while to search more carefully for ruthenium.

[1] Zeitschr. anal. Chemie, 46, 145–150, 1907.

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The final precipitate of palladium acetylide was changed to chloride, diluted, and saturated with $SO_2$ for gold, but none appeared.

Nothing else was found in the metal except a trace of copper. The iron found earlier had to be reprecipitated several times from chloride solution by ammonia to get rid of palladium. The precipitate was finally transformed into sulphate and determined volumetrically. Fe = 2.6 mg. = 0.010 per cent.

ANALYSIS OF PALLADIUM.

| | |
|---|---|
| Au | None |
| Ru | None |
| Rh | None |
| Pt | .007 |
| Ir | .008 |
| Cu | Trace |
| Zn | Doubtful trace |
| Fe | .010 |
| | 0.025 per cent. |

In the following table, the results of these analyses of metals for the temperature scale are summarized:

SUMMARIZED ANALYSES OF METALS.[1]

| Impurities stated in fractions of 1 p. ct. | Palladium. | Cobalt. | Nickel. | Copper. | Silver. | Aluminum. | Antimony. | Zinc. | Cadmium. |
|---|---|---|---|---|---|---|---|---|---|
| Pt | 0.007 | none | .0023 | [2].0011 | .0001 | | | | |
| Ir | .008 | | | | | | | | |
| Rh | none | | | | | | | | |
| Ru | none | | | | | | | | |
| Au | none | none | none | none | .0005 | | | | |
| Se | | | | none | | | | | |
| Te | | | | none | | | | | |
| As | | none | none | none | none | none | none | none | none |
| Sb | | none | none | none | none | none | | .002 | |
| Sn | | none | none | none | none | | .02(?) | | |
| Hg | | | | | none | | none | | |
| Ag | | none | none | .0006 | | | none | none | |
| Pb | none | .0176 | .0001 | none | .0008 | | trace? | .051 | .0860 |
| Bi | none | none | none | none | none | | none | none | |
| Cu | trace | .0178 | .0523 | | trace | .003 | .004 | none | trace |
| Cd | none | none | none | none | none | | none | .004 | |
| Ni | none | none | | none | none | none | none | none | none |
| Co | none | | .1063 | none | none | none | none | none | none |
| Fe | .010 | .0006 | .0042 | .0038 | .0011 | .043 | .007 | .006 | .0025 |
| Zn | trace? | none? | none? | .0007 | none? | none | none | | trace |
| Mn | | none | none | | | | none | | |
| Si | | | | none | | .190 | | none | |
| C | | | | | .0003 | .013 | | | |
| S | | .013 | none | .0020 | .0004 | .002 | trace? | none | .0005 |
| P | | | | | | none | | | |
| Ca | | | | | | none | | | |
| Na | | | | | | none | | | |
| K | | | | | | none | | | |
| Total... | .025 | .049 | .165 | .008 | .003 | .251 | .031 | .063 | .089 |

[1] A blank opposite any impurity means that it was not looked for. [2] Means platinum metals.

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## 16. THE FIXED POINTS.

### FURTHER DETAILS ON THE SUBSTANCES EMPLOYED FOR THE TEMPERATURE CONSTANTS.

*Zinc.*—Two samples of "C. P. sticks" were used, both from Eimer and Amend. No appreciable difference could be observed between their melting-points. Both melting and freezing points were sharp and measurable to a fraction of a microvolt. Successive readings did not differ by more than one microvolt. The charge was about 200 grams.

*Antimony.*—Two samples of metal were used, both from Kahlbaum, and no appreciable difference was found between their melting-points. The charge weighed about 150 grams. The melting-point is sharp and does not differ from the freezing-point by more than one microvolt, provided the undercooling which always precedes solidification does not exceed 15°. If the metal is undercooled too far to give an accurate freezing-point, the fact is easily recognized by observing that the thermo-element does not return to a sustained constant temperature, but merely rises to a maximum, then falls again. The amount of undercooling is greater the higher the metal has been heated above its melting-point after the melting is complete.

*Silver.*—The charge weighed about 260 gms. Only one supply was used. The melting and freezing points were sharp and agreed within one microvolt.

*Gold.*—A new charge of gold was used, weighing 350 grams. This was obtained from Dr. Eckfeldt of the Philadelphia Mint.

*Copper.*—The copper was obtained in the form known as "copper drops cooled in hydrogen" (Eimer and Amend). Only one supply was used. The melting and freezing points were not quite as sharp as was the case with silver, but always agreed within 1 microvolt. The temperature is very susceptible to a trace of oxide, which not only lowers the temperature appreciably, but makes it more uncertain, so that if a little oxidation has taken place it is recognizable at once. Waidner and Burgess[1] found that the best commercial electrolytic copper showed an average difference of 0.2° in the melting-point from the purified copper drops. Charge, about 210 grams.

*Diopside* (*Magnesium-calcium metasilicate*, $MgSiO_3 \cdot CaSiO_3$).—Two samples of chemically pure, artificial diopside were used, one from the preparation of Allen and White[2] and the other made up in 1909 by G. A. Rankin. No appreciable difference was found between the melting-points. No freezing-point can be obtained, as the mineral undercools considerably. The charge used was 3 grams.

*Nickel.*—A sample of specially purified electrolytic nickel was obtained from Kahlbaum. The analysis showed less than 0.2 per cent total impurities. Care must be taken in the case of nickel that no oxide forms, as a fairly sharp break can be observed about 10° below the melting-point, which may represent the eutectic of nickel and nickel oxide. This break disappeared when the nitrogen was replaced for a few minutes by hydrogen. This lower point might easily be mistaken for the melting-point of the metal, and this mistake may possibly have occurred in several of the published determinations of the melting-point of nickel. Nickel absorbs hydrogen and possibly also nitrogen, and after cooling frequently showed excrescences and signs of "spitting" such as occur with silver in air.

[1]Phys. Rev. **28**, p. 469, 1909. Bull. Bur. Stds., **6**, p. 174, 1909. [2]Am. Jour. Sci., (4), **27**, 1-47, 1909.

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*Cobalt.*—Kahlbaum's purest cobalt was used, containing less than 0.05 per cent total impurity. It was in the form of fine black powder, which was compressed into blocks for convenience in handling. The results obtained were not quite as satisfactory as with nickel on account of the higher temperature and more rapid contamination of the thermo-element. The absorption of gases seemed to be less than was the case with nickel.

Samples of Eimer and Amend's "98 to 99 per cent pure" nickel and cobalt were also tried. The difference between the two samples of nickel was not greater than the uncertainty in the melting-point caused by contamination of the thermo-element. The "98 to 99 per cent pure" cobalt melted about 3.5° lower than the pure sample. Since the impurities in nickel are usually chiefly iron and cobalt, and those of cobalt are chiefly iron and nickel, and since the melting-points of all three are close together, the melting-points of the slightly impure metals can not be expected to lie far from those of the pure metals.

*Anorthite (Aluminum-calcium silicate, $CaAl_2Si_2O_8$, or $Al_2SiO_5.CaSiO_3$).*—The anorthite used was made from pure analyzed materials by G. A. Rankin in 1909. The charge was about 3 grams. The melting-point is not quite as sharp as that of diopside. Only the melting-point can be obtained, as the mineral undercools considerably; it may even cool to glass without crystallization, in which case of course no melting-point will be obtained on the following heating.

*Palladium.*—About 350 grams of pure palladium, in the form of sheet, was loaned to us by Dr. Heraeus. It melts and freezes quite sharply, making an excellent substance for a fixed thermometric point. The greatest uncertainty is caused by the vaporization of the metal and consequent contamination of the thermo-element wire. The charges used weighed 128 and 210 grams respectively.

*Cadmium and Aluminum.*—In addition to the fixed points just described, two other metal melting-points, cadmium and aluminum, were incidentally determined. Only one measurement of the cadmium point was made on the gas thermometer, and this chiefly for the purpose of checking the extrapolation below the zinc point. The conditions of melting were the same as for zinc. The charge weighed 215 grams.

A sample of pure aluminum obtained from the Aluminum Company of America was melted in a graphite crucible of the usual size in an atmosphere of carbon monoxide. On account of the sensitiveness of aluminum to silicon contamination, the tube carrying the thermo-element was provided with a thin protecting cover of graphite, so that the metal came in contact only with pure graphite. The freezing-point was sharp and constant. The melting-point was less sharp, but lay within 0.5° of the freezing-point.

## MELTING-POINT MEASUREMENTS.

Table XIV contains in summarized form the readings of the various thermo-elements at the melting-points of the standard substances. The values are in microvolts, on the basis: Clark cell at 15° = 1.4328 volts. Each value given represents from one to six determinations of the melting and freezing points (in the case of aluminum, diopside, and anorthite, melting-points only). The thermo-element readings are given at the constant temperatures chosen to be the reference points of the nitrogen scale. Each

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element is represented by a letter (or a number in parenthesis). Thus, element C, after comparison with the gas thermometer in Table XIII, was used to determine the fixed points in Table XIV, after which it was returned to the gas-thermometer furnace for further comparison. "A" in copper read 10505 in Dec. (1908), 10502 in Jan. (1909), 10499 in Feb., 10504 in March, 10503 in May, and 10503 in June.

TABLE XIV.—THERMO-ELEMENT READINGS AT MELTING-POINTS.

| Date. | Zinc. | Antimony. | Silver. | Gold. | Copper. | Diopside. |
|---|---|---|---|---|---|---|
| 1908 | | | | | | |
| March | S 3408 | | S 9056 | | S 10476 | |
| | V 3401 | | V 9050 | | V 10477 | |
| | W 3406 | | W 9057 | | X 10485 | |
| | X 3406 | | X 9058 | | Y 10577 | |
| | Y 3437 | | Y 9147 | | Z 10438 | |
| | Z 3382 | | Z 9019 | | V 10478 | |
| | | | (42) 9066 | | | |
| | | | (32) 9081 | | | |
| April | | X 5501 | | | W 10478 | |
| | | W 5499 | | | X 10488 | |
| | | S 5503 | | | (42) 10489 | |
| | | X 5505 | | | (31) 10529 | |
| | | Y 5545 | | | | |
| | | Z 5466 | | | | |
| June | | | | | A 10500 | |
| December | S 3418 | S 5506 | S 9069 | | S 10481 | |
| | X 3411 | X 5504 | X 9071 | | X 10484 | |
| | Y 3437 | Y 5547 | Y 9151 | | Y 10581 | |
| | A 3412 | A 5507 | A 9087 | | A 10505 | |
| | (31) 3426 | | | | | |
| | (42) 3406 | | | | | |
| 1909 | | | | | | |
| January | | | | | Y 10573 | |
| | | | | | Z 10426 | |
| | | | | | A 10502 | |
| | | | | | C 10458 | |
| February | Y 3434 | Y 5541 | Y 9141 | Z 10193 | Y 10573 | |
| | Z 3382 | Z 5459 | Z 9022 | A 10260 | Z 10432 | |
| | A 3409.5 | A 5501 | A 9080 | C 10226 | A 10499 | |
| | C 3404 | C 5489 | C 9049 | D 10231 | C 10460 | |
| | D 3403 | D 5488 | D 9055 | | D 10467 | |
| March | A 3413.5 | Z 5462.5 | Z 9019 | Z 10195 | Z 10432 | |
| | C 3409.5 | A 5505.5 | A 9085 | A 10266 | A 10504 | |
| | D 3409 | C 5495 | C 9057 | C 10233 | C 10469 | |
| | | D 5495.5 | D 9059 | D 10235 | D 10473 | |
| | | | | | C 10470 | |
| | | | | | D 10475 | |
| May | | | | | Y 10571 | |
| | | | | | Z 10433 | |
| | | | | | A 10503 | |
| | | | | | D 10469 | |
| | | | | | E 10534 | |
| | | | | | F 10533 | |
| | | | | | G 10531 | |
| | | | | | $C_1$ 10454 | |
| June | | Z 5461 | Y 9137 | Z 10195 | Y 10568 | E 14230 |
| | | A 5504 | Z 9018 | A 10263 | Z 10432 | E 14226 |
| | | E 5530 | A 9082 | D 10234 | A 10503 | F 14229 |
| | | F 5530 | C 9057 | E 10295 | D 10470 | G 14229 |
| | | G 5529.5 | E 9113 | F 10296 | E 10534 | H 14231 |
| | | | F 9113 | G 10294 | F 10534 | A 14200 |
| | | | G 9111 | | G 10533 | |

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TABLE XIV.—CONTINUED.

| Nickel. | Cobalt. | Palladium | Anorthite. | Miscellaneous. |
|---|---|---|---|---|
| (Apr. 1909) | (Sept. 1909) | (Nov. 1909) | (Nov. 1909) | Cd (Mar. 1909) |
| A 14947 | E 15404[1] | H 16145 | E 16144 | Z 2465 |
| D 14883 | E 15387[1] | J 16144 | E 16151 | C 2488 |
| Z 14850 | (Oct. 1909) | J 16158 | H 16145 | D 2486 |
| A 14943 | E 15391[1] | J 16151 | F 16141 | Cd (Mar. 1910) |
| D 14881 | E 15439 | E 16143 | G 16148 | E 2502 |
| Z 14847 | F 15435 | F 16138 | C 16060 | |
| Z 14853 | G 15441 | G 16145 | | Al (Mar. 1908) |
| E 14974 | H 15436 | C 16058 | | Z 5758 |
| F 14975 | J 15445 | (Jan. 1910) | | Z 5757 |
| G 14975 | C 15359 | J 16150 | | V 5793 |
| H 14977 | A 15409 | J 16140 | | Y 5836 |
| (Sept. 1909) | | (Apr. 1911) | | |
| E 14980 | | L 16145 | | NiO-Ni (Apr. 1908) |
| F 14981 | | (Wire method) | | Z 14723 |
| G 14981 | | | | S 14750 |
| H 14983 | | | | S 14743 |
| | | | | V 14747 |
| | | | | NiO-Ni (Apr. 1909) |
| | | | | Z 14712 |
| | | | | Z 14717 |

[1]Commercial metal.

## TEMPERATURE OF THE FIXED POINTS.

Table XV contains the final temperature of each thermometric point studied. In the first column is the number of the experiment corresponding to that in Table XIII. In the second column is the correction in degrees to be applied to each of the thermo-element readings *outside* of the bulb, integrated from the readings of the auxiliary elements as described on page 66; in the third column is given the corresponding correction in microvolts. In the fourth column are the readings of the standard elements on the *outside* of the bulb, corrected as above mentioned. In the fifth column are the readings of the same thermo-elements at the fixed point in question, as obtained in the melting or freezing of metal or salt; these figures usually represent the mean of a considerable number of determinations.

In the sixth and seventh columns are the corresponding figures for the element *inside* of the bulb. In this case, however, no correction has been applied to the reading of the element, since, being located practically at the center of the bulb, it might be expected to represent the mean temperature of the entire volume of the bulb.

In the eighth and ninth columns are the temperatures of the fixed points derived from the preceding four columns. In the last column is given the weight assigned to each measurement. In assigning these weights the number of standard thermo-elements used, the amount of variation in $p_o$, and other incidental variables were taken into consideration.

As has been pointed out on page 65, the relative weights to be assigned to the inside and outside elements are different at different temperatures:

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(1) on account of the difference in contamination, and (2) on account of the fact that the inside element is subject to the influence of conduction and radiation from below. The weights assigned were as follows:

| Temperatures. | Outside elements. | Inside element. |
|---|---|---|
| 400–1100° | 3 | 1 |
| 1100–1300° | 2 | 1 |
| 1300–1550° | 1 | 1 |

The final weighted mean of the inside and outside elements is given at the head of each section of the table.

In the last section of the table are given various points which were determined to aid in interpolating between the fixed points by means of the thermo-element.[1]

The only comment which need be made here on the data in Table XV concerns the figures given under the heading "copper point." In this section of the table, the values derived at the two different initial pressures of gas in the gas thermometer (217–221 mm. and 346–347 mm.) are quoted separately in order to bring out the fact that the difference between the temperatures obtained from these two pressures is less than the experimental error. In the other sections of the table the data obtained at the two pressures are not separately arranged. Above the copper point only the low pressure was used, as the high pressure would have exceeded the range of the manometer.

[1]Since the completion of the gas-thermometer work, Dr. F. M. Jaeger has suggested to us that the melting-point of lithium silicate, which lies at 1201°, in the gap between copper (1082.6°) and diopside (1391°), would be a good calibration point for thermo-elements. He made and analyzed in this laboratory a pure sample of $Li_2SiO_3$, and determined its melting-point with one of the thermo-elements used with the gas thermometer, finding the value 1201.8°. (Not yet published.) The composition of the sample was:

| | Found. | Theoretical. |
|---|---|---|
| $SiO_2$ | 66.60 | 66.87 |
| $Li_2O$ | 32.80 | 33.13 |
| $Na_2O$ | 0.51 | |
| $K_2O$ | None | |
| FeO | None | |
| $Fe_2O_3$ | 0.016 | |
| CaO | 0.034 | |

We measured the melting-point of the same sample with another element, finding 1200.6°. Another sample, prepared by Dr. Crenshaw in this laboratory, gave 1199.6°. Its composition was:

| | |
|---|---|
| $SiO_2$ | 65.89 |
| $Li_2O$ | 32.83 |
| FeO | 0.05 |
| $H_2O$ | 1.2 |

The first sample is slightly deficient in $Li_2O$, the second is slightly deficient in $SiO_2$, and both may be taken as fairly representative of the average sample obtained by synthesis from $Li_2CO_3$ and $SiO_2$. The reproducibility of the point is probably about 1°.

The individual determinations are as follows:

| Prepared by— | Observed by— | Element. | Melting-point. |
|---|---|---|---|
| Jaeger | Jaeger | C | 1202.1° |
| Jaeger | Jaeger | C | 1201.8 |
| Jaeger | Jaeger | C | 1201.2 |
| Jaeger | Jaeger | C | 1202.0 |
| Jaeger | Jaeger | C | 1202.0 |
| Jaeger | Jaeger | C | 1201.8 |
| Jaeger | Sosman | G | 1200.6 |
| Jaeger | Sosman | G | 1200.6 |
| Crenshaw | Sosman | H | 1199.2 |
| Crenshaw | Sosman | H | 1199.8 |
| Crenshaw | Sosman | G | 1199.7 |
| Crenshaw | Sosman | G | 1199.8 |
| | | Mean | 1200.9° |

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The significance of the comparison between the inside-wound and outside-wound furnaces, which appears in the first half of the section on the copper point, has been commented on elsewhere (see p. 56).

TABLE XV.—TEMPERATURES OF THE FIXED POINTS.

| Exp. No. | Integrated correction to outside elements. | | Standard elements. | | | | Temperature. | | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| | Degrees. | M. V. | Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | By outside element. | By inside element. | |
| | | | *Zinc Point.* 418.2° | | | | | | |
| 22 | 0.0° | 0 | A 3414 | 3411 | Y 3436 | 3436 | 418.1° | 418.4° | 2 |
| 23 | −0.3 | −3 | A 3405 | 3410.5 | Y 3425 | 3435 | 418.0 | 418.4 | 2 |
| 31 | 0.0 | 0 | A 3410 | 3410.5 | Y 3436 | 3435 | 418.3 | 418.2 | 2 |
| 32 | −0.2 | −2 | A 3402 | 3410 | Y 3425 | 3434 | 418.0 | 418.1 | 2 |
| 50 | −0.1 | −0.5 | A 3413 | 3411 | ..... | ..... | 418.2 | | |
| | | | D 3405.5 | 3406 | Z 3384.5 | 3382 | 418.4 | | |
| | | | | | | | 418.3 | 418.2 | 3 |
| 73 | −0.2 | −2 | A 3401 | 3413.5 | ..... | ..... | 418.4 | | |
| | | | E 3417 | 3429 | ..... | ..... | 418.3 | | |
| | | | F 3412 | 3429 | ..... | ..... | 418.8 | | |
| | | | G 3414 | 3429 | Z 3370 | 3382 | 418.6 | | |
| | | | | | | | 418.5 | 418.3 | 4 |
| | | | | | Weighted mean, | | 418.2° | 418.3° | |
| | | | *Antimony Point.* 629.2° | | | | | | |
| 24 | −0.1 | −1 | A 5509 | 5503 | Y 5550 | 5546 | 629.2° | 629.4° | 2 |
| 25 | −0.5 | −5 | A 5496 | 5503 | Y 5529 | 5545 | 629.0 | 629.9 | 2 |
| 33 | −0.1 | −1 | A 5513 | 5503 | Y 5553 | 5544 | 629.2 | 629.3 | 2 |
| 34 | −0.5 | −5 | A 5505 | 5503 | Y 5537 | 5543 | 629.1 | 629.9 | 2 |
| 52 | −0.5 | −5 | A 5505 | 5503 | ..... | ..... | 629.6 | | |
| | | | D 5490 | 5492 | Z 5463 | 5460 | 629.2 | | |
| | | | | | | | 629.4 | 629.1 | 2 |
| 74 | −0.2 | −2 | A 5514 | 5504 | ..... | ..... | 628.2 | | |
| | | | E 5533 | 5530 | ..... | ..... | 628.8 | | |
| | | | F 5526 | 5530 | ..... | ..... | 629.5 | | |
| | | | G 5527 | 5530 | Z 5461 | 5461 | 629.4 | | |
| | | | | | | | 629.0 | 629.1 | 4 |
| 87 | −0.3 | −3 | F 5517 | 5530 | ..... | ..... | 628.9 | | |
| | | | E 5517 | 5530 | ..... | ..... | 628.9 | | |
| | | | A 5481 | 5504 | ..... | ..... | 629.9 | | |
| | | | G 5513 | 5530 | Z 5437 | 5461 | 629.3 | | |
| | | | | | | | 629.2 | 629.9 | 4 |
| | | | | | Weighted mean, | | 629.1° | 629.5° | |

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TABLE XV.—TEMPERATURES OF THE FIXED POINTS—Continued.

*Silver Point.* 960.0°

| Exp. No. | Integrated correction to outside elements. | | Standard elements. | | | | Temperature. | | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| | Degrees. | M. V. | Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | By outside element. | By inside element. | |
| 6 | +0.8 | +9 | W 9070 | 9057 | X 9100 | 9071 | 959.4° | 958.0° | 1 |
| 26 | −0.3 | −3 | A 9087 | 9083 | Y 9159 | 9141 | 959.9 | 958.6 | 2 |
| 27 | −0.8 | −9 | A 9066 | 9083 | Y 9119 | 9141 | 959.9 | 960.4 | 2 |
| 35 | −0.7 | −8 | A 9079 | 9082 | Y 9142 | 9141 | 959.7 | 959.4 | 1 |
| 36 | −0.1 | −1 | A 9097 | 9082 | Y 9163 | 9141 | 959.4 | 958.7 | 1 |
| 41 | −0.3 | −3 | A 9083 | 9081 | Y 9156 | 9141 | 959.6 | 958.5 | 2 |
| 42 | −0.8 | −9 | A 9076 | 9081 | Y 9131 | 9141 | 959.3 | 959.7 | 2 |
| 63 | −0.6 | −7 | A 9079 | 9084 | ..... | ..... | 960.7 | | |
| | | | D 9048 | 9058 | Z 9010 | 9019 | 961.2 | | |
| | | | | | | | 960.9 | 961.1 | 2 |
| 68 | −0.7 | −8 | A 9080 | 9085 | ..... | ..... | 960.3 | | |
| | | | D 9051 | 9058 | Z 9013 | 9019 | 960.4 | | |
| | | | | | | | 960.4 | 960.3 | 2 |
| 76 | −0.2 | −2 | A 9088 | 9082 | ..... | ..... | 959.2 | | |
| | | | E 9112 | 9113 | ..... | ..... | 959.7 | | |
| | | | F 9097 | 9113 | ..... | ..... | 961.2 | | |
| | | | G 9106 | 9111 | Z 9002 | 9018 | 960.2 | | |
| | | | | | | | 960.1 | 961.2 | 4 |
| 81 | +0.3 | +3 | F 9132 | 9113 | ..... | ..... | 959.5 | | |
| | | | E 9131 | 9113 | ..... | ..... | 959.6 | | |
| | | | A 9083 | 9082 | ..... | ..... | 961.1 | | |
| | | | G 9125 | 9111 | Z 9015 | 9018 | 960.0 | | |
| | | | | | | | 960.0 | 961.5 | 4 |
| 88 | +0.3 | +3 | F 9143 | 9113 | ..... | ..... | 959.0 | | |
| | | | E 9139 | 9113 | ..... | ..... | 959.4 | | |
| | | | A 9093 | 9082 | ..... | ..... | 960.7 | | |
| | | | G 9135 | 9111 | Z 9036 | 9018 | 959.6 | | |
| | | | | | | | 959.7 | 960.1 | 4 |
| | | | | | Weighted mean, | | 959.9° | 960.2° | |

*Gold Point.* 1062.4°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 64 | −0.3 | −3 | A 10262 | 10265 | ..... | ..... | 1062.4° | | |
| | | | D 10226 | 10233 | Z 10178 | 10193 | 1062.8 | | |
| | | | | | | | 1062.6 | 1063.4° | 2 |
| 69 | −0.4 | −4 | A 10253 | 10266 | ..... | ..... | 1061.4 | | |
| | | | D 10217 | 10234 | Z 10169 | 10193 | 1061.7 | | |
| | | | | | | | 1061.6 | 1062.3 | 2 |
| 77 | −0.3 | −3 | A 10255 | 10263 | ..... | ..... | 1061.2 | | |
| | | | E 10282 | 10295 | ..... | ..... | 1061.6 | | |
| | | | F 10263 | 10296 | ..... | ..... | 1063.4 | | |
| | | | G 10276 | 10294 | Z 10161 | 10193 | 1062.1 | | |
| | | | | | | | 1062.1 | 1063.3 | 4 |

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TABLE XV.—TEMPERATURES OF THE FIXED POINTS—Continued.

*Gold Point.* 1062.4°—Continued.

| Exp. No. | Integrated correction to outside elements. Degrees. | M. V. | Standard elements. Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | Temperature. By outside element. | By inside element. | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| 82 | +0.4 | +4 | F 10303 | 10296 | ..... | ..... | 1061.9° | | |
| | | | E 10304 | 10295 | ..... | ..... | 1061.8 | | |
| | | | A 10256 | 10263 | ..... | ..... | 1063.1 | | |
| | | | G 10296 | 10294 | Z 10181 | 10193 | 1062.4 | | |
| | | | | | | | 1062.3 | 1063.6° | 4 |
| | | | | | Weighted mean, | | 1062.2° | 1063.2° | |
| | *Copper Point.* 1082.6° (*Lower Pressure.* $p_0$ = 217–221 mm.) | | | | | | | | |
| 2 | +1.2 | +14 | W 10457 | 10478 | X 10491 | ..... | 1081.7° | ..... | 1 |
| 9 | +1.0 | +12 | W 10495 | 10478 | X 10555 | ..... | 1082.2 | ..... | 1 |
| 11 | +1.2 | +14 | W 10487 | 10478 | X 10512 | ..... | 1083.1 | ..... | 1 |
| 18 | +0.7 | + 8 | A 10510 | 10502 | Y 10612 | 10573 | 1082.2 | ..... | 2 |
| 19 | −0.4 | − 5 | A 10501 | 10502 | Y 10584 | 10573 | 1082.0 | 1081.0° | 3 |
| 20 | −0.8 | − 9 | A 10488 | 10502 | Y 10555 | 10573 | 1082.1 | 1082.5 | 3 |
| 28 | −0.3 | − 4 | A 10512 | 10501 | Y 10593 | 10573 | 1082.1 | 1081.4 | 3 |
| 29 | −0.9 | −10 | A 10494 | 10501 | Y 10556 | 10573 | 1082.2 | 1083.0 | 3 |
| 37 | −0.6 | − 7 | A 10504 | 10501 | Y 10576 | 10573 | 1082.0 | 1082.0 | 2 |
| 38 | −0.3 | − 4 | A 10509 | 10500 | Y 10585 | 10573 | 1082.2 | 1081.9 | 2 |
| 39 | +0.7 | + 8 | A 10517 | 10500 | Y 10617 | ..... | 1082.3 | ..... | 2 |
| 43 | −0.3 | − 4 | A 10512 | 10500 | Y 10595 | 10573 | 1082.2 | 1081.3 | 3 |
| 44 | −0.9 | −10 | A 10501 | 10499 | Y 10568 | 10573 | 1082.0 | 1082.6 | 3 |
| 45 | +0.6 | + 7 | A 10515 | 10499 | Y 10617 | ..... | 1082.3 | ..... | 2 |
| 89 | +0.5 | + 6 | F 10546 | 10534 | ..... | ..... | 1081.8 | | |
| | | | E 10544 | 10534 | ..... | ..... | 1081.9 | | |
| | | | A 10496 | 10503 | ..... | ..... | 1083.4 | | |
| | | | G 10538 | 10533 | Z 10428 | 10432 | 1082.4 | | |
| | | | | | | | 1082.4 | 1083.1 | 4 |
| 126[1] | +0.4 | + 5 | E 10631 | 10534 | ..... | ..... | 1082.2 | | |
| | | | F 10627 | 10534 | ..... | ..... | 1082.6 | | |
| | | | G 10621 | 10533 | ..... | ..... | 1083.0 | | |
| | | | H 10623 | 10535 | C 10567 | 10470 | 1083.0 | | |
| | | | | | | | 1082.7 | 1082.5 | 4 |
| | | | | | Weighted mean, | | 1082.2° | 1082.2° | |
| | *Copper Point*—(*Higher Pressure.* $p_0$ = 346–347 mm.) | | | | | | | | |
| 60 | −0.7 | −8 | A 10500 | 10502 | ..... | ..... | 1083.4° | | |
| | | | D 10465 | 10470 | Z 10422 | 10432 | 1083.6 | | |
| | | | | | | | 1083.5 | 1084.1° | 1 |
| 65 | −0.8 | −9 | A 10502 | 10503 | ..... | ..... | 1083.0 | | |
| | | | D 10465 | 10471 | Z 10420 | 10432 | 1083.4 | | |
| | | | | | | | 1083.2 | 1083.9 | 2 |
| 70 | −0.3 | −4 | A 10508 | 10504 | ..... | ..... | 1082.4 | | |
| | | | D 10475 | 10472 | Z 10444 | 10432 | 1082.6 | | |
| | | | | | | | 1082.5 | 1081.8 | 2 |

[1]Made with outside-wound furnace. See page 56 and Fig. 10.

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TABLE XV.—TEMPERATURES OF THE FIXED POINTS—Continued.

*Copper Point.* (*Higher Pressure.* $p_0 = 346$–$347$ mm.)—Continued.

| Exp. No. | Integrated correction to outside elements. | | Standard elements. | | | | Temperature. | | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| | Degrees. | M. V. | Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | By outside element. | By inside element. | |
| 78 | −0.1 | −1 | A 10502 | 10503 | ..... | | 1081.4° | | |
| | | | E 10528 | 10534 | ..... | | 1081.8 | | |
| | | | F 10509 | 10534 | ..... | | 1083.4 | | |
| | | | G 10522 | 10533 | Z 10404 | 10432 | 1082.3 | | |
| | | | | | | | 1082.2 | 1083.7° | 4 |
| 83 | +0.1 | +1 | F 10535 | 10534 | ..... | | 1082.1 | | |
| | | | E 10535 | 10534 | ..... | | 1082.1 | | |
| | | | A 10488 | 10503 | ..... | | 1083.5 | | |
| | | | G 10527 | 10533 | Z 10403 | 10432 | 1082.7 | | |
| | | | | | | | 1082.6 | 1084.6 | 4 |
| 84 | +0.7 | +8 | F 10544 | 10534 | ..... | | 1082.0 | | |
| | | | E 10542 | 10534 | ..... | | 1082.3 | | |
| | | | A 10493 | 10503 | ..... | | 1083.8 | | 4 |
| | | | G 10533 | 10533 | Z 10426 | 10432 | 1083.0 | | |
| | | | | | | | 1082.8 | 1083.5 | |
| | | | | | Weighted mean, | | 1082.7° | 1083.7° | |
| | | | | | Mean of 2 pressures, | | 1082.5° | 1082.9° | |
| | | | *Diopside Point.* 1391.2° | | | | | | |
| 96 | 0.0 | 0 | E 14227 | 14228 | ..... | | 1392.1° | | |
| | | | F 14222 | 14229 | ..... | | 1392.5 | | |
| | | | G 14245 | 14229 | ..... | | 1390.7 | | |
| | | | H 14251 | 14231 | Z 14121 | 14103 | 1390.4 | | |
| | | | | | | | 1391.4 | 1390.5° | 1 |
| 97 | +1.0 | +13 | E 14260 | 14228 | ..... | | 1392.4 | | |
| | | | F 14254 | 14229 | ..... | | 1393.0 | | |
| | | | G 14287 | 14229 | ..... | | 1390.4 | | |
| | | | H 14295 | 14231 | Z 14156 | 14103 | 1389.9 | | |
| | | | | | | | 1391.4 | 1390.5 | 1 |
| 99 | −0.1 | −1 | E 14213 | 14228 | ..... | | 1394.5 | | |
| | | | F 14195 | 14229 | ..... | | 1396.0 | | |
| | | | G 14215 | 14229 | ..... | | 1394.4 | | |
| | | | H 14212 | 14231 | Z 14099 | 14103 | 1394.8 | | |
| | | | | | | | 1394.9 | 1393.7 | 1 |
| 100 | +0.7 | +9 | E 14251 | 14228 | ..... | | 1394.4 | | |
| | | | F 14244 | 14229 | ..... | | 1395.0 | | |
| | | | G 14268 | 14229 | ..... | | 1393.1 | | |
| | | | H 14273 | 14231 | Z 14156 | 14103 | 1392.9 | | |
| | | | | | | | 1393.8 | 1391.8 | 1 |

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TABLE XV.—TEMPERATURES OF THE FIXED POINTS—Continued.

*Diopside Point.* 139 2°—Continued.

| Exp. No. | Integrated correction to outside elements. Degrees. | M. V. | Standard elements. Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | Temperature. By outside element. | By inside element. | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| 103 | −0.4 | − 5 | E 14211 | 14228 | ..... | ..... | 1392.5° | | |
| | | | F 14204 | 14229 | ..... | ..... | 1393.1 | | |
| | | | G 14217 | 14229 | ..... | ..... | 1392.1 | | |
| | | | H 14230 | 14231 | Z 14124 | 14103 | 1391.2 | | |
| | | | | | | | 1392.2 | 1389.4° | 3 |
| 104 | +1.0 | +13 | E 14242 | 14228 | ..... | ..... | 1392.5 | | |
| | | | F 14212 | 14229 | ..... | ..... | 1394.9 | | |
| | | | G 14249 | 14229 | ..... | ..... | 1392.0 | | |
| | | | H 14262 | 14231 | Z 14155 | 14103 | 1391.1 | | |
| | | | | | | | 1392.6 | 1389 3 | 3 |
| 106 | −0.6 | − 8 | E 14228 | 14228 | ..... | ..... | 1391.7 | | |
| | | | F 14225 | 14229 | ..... | ..... | 1392.0 | | |
| | | | G 14233 | 14229 | ..... | ..... | 1391.3 | | |
| | | | H 14243 | 14231 | Z 14123 | 14103 | 1390.7 | 1390.0 | 2 |
| | | | | | | | 1391.4 | | |
| 107 | +0.9 | +12 | E 14248 | 14228 | ..... | ..... | 1391.9 | | |
| | | | F 14237 | 14229 | ..... | ..... | 1392.8 | | |
| | | | G 14245 | 14229 | ..... | ..... | 1392.2 | | |
| | | | H 14252 | 14231 | Z 14152 | 14103 | 1391.8 | 1389.4 | 2 |
| | | | | | | | 1392.2 | | |
| 130 | −0.6 | − 7 | E 14243 | 14228 | ..... | ..... | 1390.2 | | |
| | | | F 14241 | 14230 | ..... | ..... | 1390.6 | | |
| | | | G 14249 | 14230 | ..... | ..... | 1389.9 | | |
| | | | H 14239 | 14228 | C 14146 | 14153 | 1390.6 | | |
| | | | | | | | 1390.3 | 1392.0 | 3 |
| | | | | | Weighted mean, | | 1392.0° | 1390.4° | |

*Nickel Point.* 1452.3°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 109 | +0.7 | + 8 | E 15028 | 14977 | ..... | ..... | 1451.2° | | |
| | | | H 15027 | 14980 | Z 14903 | 14850 | 1451.6 | | |
| | | | | | | | 1451.4 | 1451.1° | 1 |
| 111 | 0 | 0 | E 14980 | 14977 | ..... | ..... | 1453.2 | | |
| | | | H 14978 | 14980 | Z 14867 | 14850 | 1453.7 | | |
| | | | | | | | 1453.5 | 1452.1 | 2 |
| 112 | +0.9 | +11 | E 14971 | 14977 | ..... | ..... | 1453.8 | | |
| | | | F 14958 | 14978 | ..... | ..... | 1454.9 | | |
| | | | H 14991 | 14980 | Z 14872 | 14850 | 1452.4 | | |
| | | | | | | | 1453.7 | 1451.5 | |

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TABLE XV.—TEMPERATURES OF THE FIXED POINTS—Continued.

*Nickel Point.* 452 3°—Continued.

| Exp. No. | Integrated correction to outside elements. Degrees. | M. V. | Standard elements. Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | Temperature. By outside element. | By inside element. | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| 123 | −0.6 | − 7 | E 14984 | 14977 | ..... | ..... | 1454.3° | | |
| | | | F 14989 | 14978 | A 14982 | 14945 | 1453.9 | | |
| | | | | | | | 1454.1 | 1451.8° | 2 |
| 124 | +0.8 | +10 | E 14989 | 14977 | ..... | ..... | 1454.6 | | |
| | | | F 14994 | 14978 | A 14996 | 14945 | 1454.3 | | |
| | | | | | | | 1454.5 | 1451.5 | 1 |
| 133 | −0.3 | − 4 | E 14954 | 14977 | ..... | ..... | 1451.9 | | |
| | | | F 14958 | 14976 | ..... | ..... | 1451.5 | | |
| | | | G 14955 | 14981 | ..... | ..... | 1452.2 | | |
| | | | H 14946 | 14977 | C 14882 | 14898 | 1452.5 | | |
| | | | | | | | 1452.0 | 1451.3 | 4 |
| | | | | | Weighted mean, | | 1453.0° | 1451.6° | |
| | | | *Cobalt Point.* 1489.8° | | | | | | |
| 115 | +0.1 | + 1 | E 15390 | 15439 | ..... | ..... | 1488.7° | | |
| | | | F 15375 | 15435 | A 15357 | 15409 | 1489.6 | | |
| | | | | | | | 1489.1 | 1488.9° | 3 |
| 116 | +1.4 | +17 | E 15428 | 15439 | ..... | ..... | 1490.5 | | |
| | | | F 15434 | 15435 | ..... | ..... | 1489.7 | | |
| | | | G 15435 | 15441 | A 15421 | 15409 | 1490.1 | | |
| | | | | | | | 1490.1 | 1488.6 | 3 |
| 118 | −0.5 | − 6 | E 15385 | 15439 | ..... | ..... | 1491.7 | | |
| | | | F 15383 | 15435 | ..... | ..... | 1491.6 | | |
| | | | G 15393 | 15441 | A 15382 | 15409 | 1491.3 | | |
| | | | | | | | 1491.5 | 1489.6 | 2 |
| 120 | −0.4 | − 5 | E 15381 | 15439 | ..... | ..... | 1491.7 | | |
| | | | F 15371 | 15435 | ..... | ..... | 1492.1 | | |
| | | | G 15363 | 15441 | A 15379 | 15409 | 1493.3 | | |
| | | | | | | | 1492.7 | 1489.4 | 1 |
| 121 | +0.7 | + 9 | E 15406 | 15439 | ..... | ..... | 1492.0 | | |
| | | | F 15405 | 15435 | ..... | ..... | 1491.8 | | |
| | | | G 15398 | 15441 | A 15412 | 15409 | 1492.8 | | |
| | | | | | | | 1492.2 | 1489.1 | 1 |
| | | | | | Weighted mean, | | 1490.6° | 1489.0° | |
| | | | *Palladium Point.* 1549.2° | | | | | | |
| 134 | −0.7 | − 9 | E 16151 | 16143 | ..... | ..... | 1549.5° | | |
| | | | F 16161 | 16138 | ..... | ..... | 1548.3 | | |
| | | | G 16139 | 16145 | ..... | ..... | 1550.6 | | |
| | | | H 16147 | 16145 | C 16075 | 16058 | 1550.1 | | |
| | | | | | | | 1549.6° | 1548.8° | |

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TABLE XV.—TEMPERATURES OF THE FIXED POINTS—Continued.

*Anorthite Point.* 1549.5°.

| Exp. No. | Integrated correction to outside elements. Degrees. | M. V. | Standard elements. Outside corrected. | Fixed point. | Inside uncorrected. | Fixed point. | Temperature. By outside element. | By inside element. | Weight. |
|---|---|---|---|---|---|---|---|---|---|
| 134 | −0.7 | −9 | E 16151 | 16148 | ..... | | 1549.9° | | |
| | | | F 16161 | 16141 | ..... | | 1548.6 | | |
| | | | G 16139 | 16148 | ..... | | 1550.9 | | |
| | | | H 16147 | 16145 | C 16075 | 16060 | 1550.0 | | |
| | | | | | | | 1549.9° | 1549.0° | |
| | | | *Interpolation Points.* | | | | | | |
| 49 | −0.1 | −1 | A 2486 | 2492 | ..... | | 320.2° | | |
| | | | D 2482 | 2486 | Z 2462 | 2465 | 320.0 | | |
| | | | | | | | 320.1° | 319.9° | |
| | | | | | Mean for cadmium, | | 320.0° | | |
| 51 | 0.0 | 0 | A 4451 | 4450 | ..... | | 524.6 | | |
| | | | D 4439 | 4442 | Z 4413 | 4417 | 525.0 | | |
| | | | | | | | 524.8° | 525.1 | |
| | | | | | Mean for A=4450, | | 524.9° | | |
| 62 | 0.0 | 0 | A 7895 | 7900 | ..... | | 854.2 | | |
| | | | D 7869 | 7881 | Z 7829 | 7848 | 854.9 | | |
| | | | | | | | 854.6° | 855.5 | |
| 67 | −0.2 | −2 | A 7883 | 7900 | ..... | | 854.0 | | |
| | | | D 7859 | 7881 | Z 7820 | 7848 | 854.5 | | |
| | | | | | | | 854.3° | 855.0 | |
| | | | | | Mean for A=7900, | | 854.7° | | |
| 128 | −0.2 | −2 | E 12004 | 12000 | ..... | | 1206.3 | | |
| | | | F 12001 | 12001 | ..... | | 1206.7 | | |
| | | | G 12008 | 12001 | ..... | | 1206.1 | | |
| | | | H 12000 | 12003 | C 11914 | 11928 | 1206.9 | | |
| | | | | | | | 1206.5° | 1207.8 | |
| 132 | +0.1 | +1 | E 11947 | 12000 | ..... | | 1206.0 | | |
| | | | F 11952 | 11997 | ..... | | 1205.3 | | |
| | | | G 11950 | 12001 | ..... | | 1205.8 | | |
| | | | H 11941 | 12003 | C 11887 | 11928 | 1206.8 | | |
| | | | | | | | 1206.0° | 1205.0 | |
| | | | | | Mean for E=12000, | | 1206.4° | | |
| 129 | −0.6 | −5 | E 13107 | 13100 | ..... | | 1297.4 | | |
| | | | F 13102 | 13101 | ..... | | 1297.9 | | |
| | | | G 13110 | 13101 | ..... | | 1297.2 | | |
| | | | H 13101 | 13103 | C 13007 | 13023 | 1298.1 | | |
| | | | | | | | 1297.7° | 1299.3 | |
| | | | | | Mean for E=13100, | | 1298.5° | | |

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## 17. INTERPOLATION BETWEEN THE FIXED POINTS.

The preparation of formulæ to represent the relation between the temperature defined by the gas thermometer and the electromotive force of a thermo-element has always been a cause of considerable dissatisfaction, both to the maker and the user. The chief reason for this is perhaps the fact that the formulæ used have been applicable only to limited portions of the curve and have therefore given no suggestion of physical significance. In the Reichsanstalt publication[1] the data extended from 300° to 1100° and included several good fixed points (melting-points of pure metals) between which no interpolation, however rough, could go far astray. Accordingly, in so far as interpolation was concerned, but little attention required to be given to the formulation of this relation. It was sufficient that a simple formula of the form

$$e = -a + bt + ct^2$$

could be made to represent the observations between 300° and 1100° within the limits of errors of observation.

If the investigator's responsibility could be made to end with the representation of his own observations, no serious difficulty would arise, but such a formula when published is placed in the hands of many who do not realize that no physical significance was attached to the formula by its author and that its extrapolation in either direction would be fraught with grave danger. A mere inspection of the equation is sufficient to show that the electromotive force does not become zero for zero temperature, thereby immediately proving that extrapolation downward does not correspond to the observed readings of the thermo-element. In the Reichsanstalt equation this constant term was in fact sufficiently large to lead to absurdities if the extrapolation was continued far below 300°.

Notwithstanding the warning contained in this situation, extrapolation upward of the thermo-electric curve has been employed almost universally for the determination of temperatures above 1100°, not only for direct determinations of temperature with the thermo-element itself, but also for the calibration of optical pyrometric apparatus. The absence of absolute determinations in this region has left this practice in undisturbed security until recently, when some doubt has been thrown upon the validity of irresponsible upward extrapolation by various observations:

(1) The increase in the accuracy now attainable with the optical pyrometer has given an independent thermal scale comparable with that of the thermo-element and overlapping the same region. The two curves have not been found to correspond.

(2) Experimental determinations of the melting-point of platinum by continuing observations of the thermo-element up to a point where a portion of its platinum wire melts, have been undertaken in the national laboratories of Germany, England, and the United States, and have yielded a value measured upon the extrapolated thermo-electric curve of about 1710°. The agreement in the different determinations was good and the result found general acceptance for a time. More recently, as has been stated,

[1] Holborn and Day, 1900, loc. cit.

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Holborn and Valentiner have made successful measurements with the gas thermometer at the temperature of melting palladium, and although high accuracy was not attempted, it became clear that the palladium point obtained by extrapolating with the thermo-element was much too low and by inference the platinum point even more so, for the various optical methods give opportunity for a very good determination of the temperature difference between the melting-points of the two metals. The most recent estimates of the platinum melting-point obtained in this way have placed it between 1750° and 1755°, indicating that the upward extrapolation with the thermo-element has given rise to an error of about 45° at the platinum point (see following table.)

The data obtained in the present investigation throw much light upon this situation. If we take the observations of our series over the range covered by the Reichsanstalt scale (300° to 1100°) and write an equation for these of the same type as that used at the Reichsanstalt, it will read

$$e = -302 + 8.2356t + .0016393t^2$$

and this equation will reproduce the temperatures of the standard melting-points which fall in this region with a maximum error of 3 microvolts (= 0.3°), an accuracy far within the errors of observation. But if we extrapolate this curve in accordance with the general practice above described, and compare the resulting electromotive forces with our observations between 1100° and the melting-point of platinum, a somewhat startling surprise awaits us. Although the curve below the copper point is a practically perfect reproduction of the observations, it diverges from the gas-thermometer scale at the melting-point of palladium by 248 microvolts, which represents a temperature error of 20°. At the platinum melting-point it has grown to 45°. This comparison is made in the table below.

| | Temp. | Observed. | Calculated. | Observed–Calculated | Observed—Calculated. |
|---|---|---|---|---|---|
| | ° | *mv.* | *mv.* | *mv.* | ° |
| Zinc | 418.2 | 3429 | 3429 | 0 | 0.0 |
| Antimony | 629.2 | 5530 | 5530 | 0 | 0.0 |
| Silver | 960.0 | 9113 | 9115 | −2 | −0.2 |
| Gold | 1062.4 | 10295 | 10298 | −3 | −0.3 |
| Copper | 1082.6 | 10534 | 10534 | 0 | 0.0 |
| | | | *Extrapolation.* | | |
| | 1206.4 | 12000 | 12019 | − 19 | − 1.6 |
| | 1298.5 | 13100 | 13156 | − 56 | − 4.7 |
| Diopside | 1391.2 | 14228 | 14328 | −100 | − 8.3 |
| Nickel | 1452.3 | 14977 | 15116 | −139 | −11.5 |
| Cobalt | 1489.8 | 15439 | 15606 | −167 | −13.8 |
| Palladium | 1549.2 | 16143 | 16391 | −248 | −20.6 |
| Platinum | (1752.)[1] | 18616 | 19159 | −543 | −45.3 |

If, on the other hand, we represent $t$ as a function of $e$, using the same data as before, the equation will take the form

$$t = 47.2 + 0.11297e - 1.3946\ (10)^{-6}e^2$$

[1]Values in parenthesis extrapolated (see p. 113).

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This curve passes through the fixed points below 1100°, nearly as accurately as the previous one, and is also quite competent to interpolate temperatures through the range of the old standard scale. Extrapolating this in turn up to the platinum point and comparing it with our gas-thermometer measurements in the higher region leads to temperatures about 42° too low for palladium and 85° too low for platinum.

| | Observed. | Calculated. | Observed—Calculated. |
|---|---|---|---|
| | ° | ° | ° |
| Zinc | 418.2 | 418.2 | 0.0 |
| Antimony | 629.2 | 629.3 | −0.1 |
| Silver | 960.0 | 960.9 | −0.9 |
| Gold | 1062.4 | 1062.4 | 0 |
| Copper | 1082.6 | 1082.5 | +0.1 |
| | *Extrapolation.* | | |
| | 1206.4 | 1202.0 | + 4.4 |
| | 1298.5 | 1287.8 | +10.7 |
| Diopside | 1391.2 | 1372.2 | +19.0 |
| Nickel | 1452.3 | 1426.3 | +26.0 |
| Cobalt | 1489.8 | 1458.9 | +30.9 |
| Palladium | 1549.2 | 1507.4 | +41.8 |
| Platinum | (1752.) | 1667. | +85. |

The untrustworthiness of the present practice of extending thermo-element values obtained below 1100° into the region above that temperature is therefore abundantly demonstrated.

We were unable to find a simple parabola with which to represent the whole series of observations between 300° and 1550° within the errors of observation. The simplest procedure is therefore to divide the long curve into two parts. This plan is carried out below in the form in which it will probably be found most useful. A parabola passing through zinc, antimony and copper reproduces the results over that temperature range within the errors of observation. A similar parabola through copper, diopside, and palladium gives the upper temperatures as accurately as they were measured. These two equations offer a means of safe and convenient interpolation throughout the entire range of gas-thermometer measurements. In this series are included certain gas-thermometer measurements given at the end of Table XV, which were made at temperatures between the fixed melting-points, for the purpose of checking the interpolation formula, together with a single gas-thermometer determination of the cadmium melting-point and the extrapolated platinum point described on p. 115. The temperature 854.1 appears here corrected by −0.6°, since the series, of which this measurement formed a part, showed a systematic difference of about this amount from the final average of antimony and silver, which lie on either side of this point.

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CADMIUM TO COPPER. $e = -302 + 8.2356t + .0016393t^2$

| | Temperature. | Observed. | Calculated. | Observed—Calculated | Observed—Calculated. |
|---|---|---|---|---|---|
| | ° | *mv.* | *mv.* | *mv.* | ° |
| Cadmium | 320.0 | 2502 | 2501 | +1 | +0.1 |
| Zinc | 418.2 | 3429 | 3429 | 0 | 0.0 |
| | 524.9 | 4470 | 4472 | −2 | −0.2 |
| Antimony | 629.2 | 5530 | 5530 | 0 | 0.0 |
| | 854.1 | 7929 | 7928 | +1 | +0.1 |
| Silver | 960.0 | 9113 | 9115 | −2 | −0.2 |
| Gold | 1062.4 | 10295 | 10298 | −3 | −0.3 |
| Copper | 1082.6 | 10534 | 10534 | 0 | 0.0 |

COPPER TO PALLADIUM. $e = -1941 + 11.1746t + .00032161t^2$

| | | | | | |
|---|---|---|---|---|---|
| Copper | 1082.6 | 10534 | 10534 | 0 | 0.0 |
| | 1206.4 | 12000 | 12008 | − 8 | −0.7 |
| | 1298.5 | 13100 | 13111 | −11 | −0.9 |
| Diopside | 1391.2 | 14228 | 14228 | 0 | 0.0 |
| Nickel | 1452.3 | 14977 | 14967 | +10 | +0.8 |
| Cobalt | 1489.8 | 15439 | 15421 | +18 | +1.5 |
| Palladium | 1549.2 | 16143 | 16143 | 0 | 0.0 |
| Platinum | (1752.) | 18616 | 18624 | − 8 | −0.7 |

It is possible to write a cubic equation which will reproduce the entire series from zinc to palladium without error greater than the normal accuracy of the observations themselves, but even this equation goes astray at the platinum point by 5°, and reminds us again of the absence of physical significance in all these formulæ. The equation offered makes no pretensions to a least-square solution with balanced residuals, but is arranged so that the greatest uncertainties are found in that portion of the curve where the greatest experimental error lies. The coefficients were rounded off for convenience of computation.

CADMIUM TO PALLADIUM. $e = -169 + 7.57t + 0.002648t^2 - 0.0000004724t^3$

| | Temp. | Observed. | Calculated. | Observed—Calculated. | Observed—Calculated. |
|---|---|---|---|---|---|
| | ° | *mv.* | *mv.* | *mv.* | ° |
| Cadmium | 320.0 | 2502 | 2509 | − 7 | −0.8 |
| Zinc | 418.2 | 3429 | 3425 | + 4 | +0.4 |
| | 524.9 | 4470 | 4466 | + 4 | +0.4 |
| Antimony | 629.2 | 5530 | 5525 | + 5 | +0.5 |
| | 854.1 | 7929 | 7934 | − 5 | −0.5 |
| Silver | 960.0 | 9113 | 9121 | − 8 | −0.7 |
| Gold | 1062.4 | 10295 | 10296 | − 1 | −0.1 |
| Copper | 1082.6 | 10534 | 10530 | + 4 | +0.3 |
| | 1206.4 | 12000 | 11988 | +12 | +1.0 |
| | 1298.5 | 13100 | 13091 | + 9 | +0.7 |
| Diopside | 1391.2 | 14228 | 14215 | +13 | +1.1 |
| Nickel | 1452.3 | 14977 | 14963 | +14 | +1.2 |
| Cobalt | 1489.8 | 15439 | 15424 | +15 | +1.2 |
| Palladium | 1549.2 | 16143 | 16157 | −14 | −1.2 |
| Platinum | 1752. | 18616 | 18681 | −65 | −5.4 |

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## 18. EXTRAPOLATION UPWARD. MELTING-POINT OF PLATINUM.

Now that the gas thermometer has given us measured temperatures up to 1550°, the extrapolation out to the platinum melting-point, which in recent years has been variously estimated at from 1710° (Harker) to 1855° (Barus), should at least become more certain than heretofore. To extrapolate 200° beyond the upper limit of a curve which has been measured from 300° to 1550° is a task of quite different character from the one hitherto undertaken of extrapolating 650° beyond a measured curve which stopped at 1100°.

Two methods are available and convenient for making this extrapolation:

(1) To continue observations of the electromotive force of the thermo-element until the platinum wire melts.

(2) To employ one of the radiation pyrometers to measure the temperature interval from palladium to platinum.

The first method is the most sensitive one available in this temperature region and inasmuch as we had been using it continuously and successfully for purposes of interpolation, the opportunity seemed favorable for adding as good an estimate of this classical temperature point as the rather unusual facilities at our disposal permitted. Platinum, like gold, offers an ideal fixed temperature during melting. The melting-point is sharp, it can be determined in air without fear of oxidation or contamination either from the atmosphere or from contact with lime, magnesia, or stable silicates. Moreover, the purity of platinum is so readily checked by its physical properties (electromotive force in thermo-elements, temperature coefficient of conductivity) that there is hardly a possibility of uncertainty from this cause. The present determinations were made by melting the platinum wire of Heraeus thermo-elements of which the recorded electromotive force will afford a sufficient guarantee of its purity. The impurities contained in these wires are hardly determinable quantitatively by chemical means.

Each thermo-element was heated gradually up to the melting-point of the platinum wire, within a glazed Marquardt porcelain tube, in the region of maximum temperature of a resistance furnace of the carbon tube type.[1] Carbon monoxide around the outside of the porcelain tube protected the furnace from oxidation, and a current of dry air in the inside prevented contamination of the thermo-element. Both wires of the element were inclosed in Marquardt capillaries, leaving only about 2 mm. of the platinum exposed next to the junction. It was always this portion that melted, the point being marked by a halt of about one minute in the gradual rise in temperature of the element, preceding the formation of a globule and the interruption of the circuit. New Marquardt tubes were used for each determination. Several elements were examined for contamination after the measurement,[2] and no appreciable amount was found. A vertical section of the furnace is shown in Fig. 14.

In Table XVI are given the experimental results. The values are in microvolts, corrected as before.[3] The silver point, being about half way

[1] S. A. Tucker, Trans. Amer. Electrochem. Soc., 11, 303-306, 1907.
[2] Method described on p. 64.
[3] Page 63.

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between 0° and platinum, is included in order to indicate the general course of the interpolation curve.

With these are included the results obtained by other observers with similar 10 per cent rhodium alloys. Harker[1] measured the E. M. F. at the melting-point of the platinum wire in a resistance furnace of refractory oxides. Waidner and Burgess[2] made similar measurements in connection with their optical determination of the melting-point of platinum. Their figures, being in terms of the United States legal volt (Clark at 15° = 1.434) have been corrected to the true volt (Clark at 15° = 1.4328). Other investigators (Holborn and Henning,[3] Nernst and von Wartenberg,[4] Holborn and Valentiner[5]) have measured the melting-point of platinum in various ways, but without recording the thermo-electric data.

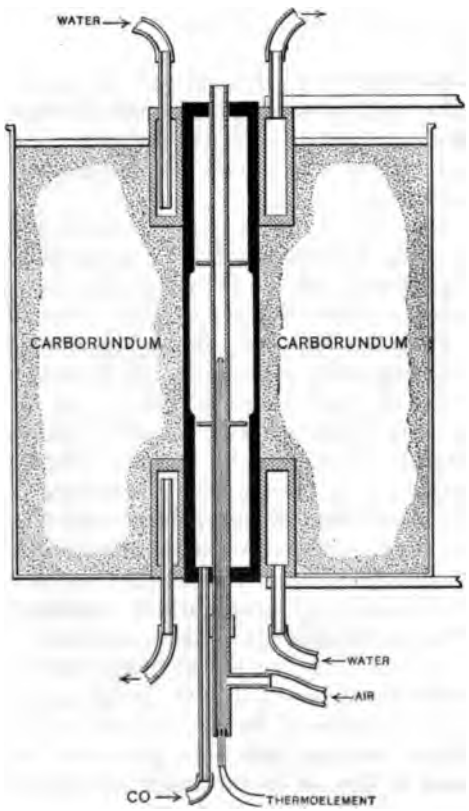


FIG. 14. Carbon-tube furnace for melting-point of platinum. Scale, 1 : 4.

In general, the curves for all the different 10 per cent elements, both our own and those of other observers, are similar in form, and the divergence of each from the mean increases with increasing temperature. In this connection it should be remarked that the E. M. F. at the palladium point (16140 microvolts) obtained by Holborn and Valentiner with an element whose gold point was 10295, agrees almost exactly with a similar element from our series, with a gold point of 10295 and palladium point of 16143. The disagreement between various observers as to the melting-points of these metals is, then, not so much a matter of purity of metals or accuracy of thermo-electric measurements, as it is of the evaluation of these in terms of the nitrogen thermometer.

We have extrapolated the curves of our own elements, on which we have complete data, using for this purpose the portion of the curve from 1100° to 1550°. A parabola passed through the melting-points of copper (1082.6°), diopside (1391.2°), and palladium (1549.2°), gives, in the case of the various 10 per cent elements, values for platinum from 1748° to 1753°; the 1 per

[1] J. A. Harker, Proc. Roy. Soc., **76**, A, 235–250, 1905.
[2] C. W. Waidner and G. K. Burgess, Bull. Bur. Standards, vol 3, p. 200, 1907.
[3] L. Holborn and F. Henning, Sitzb. Berl. Akad., 1905, 311–317.
[4] W. Nernst and H. von Wartenberg, Ber. Deut. Phys. Ges., 4, 48–58, 1906.
[5] L. Holborn and S. Valentiner, Ann. Phys. (4), **22**, 1–48, 1907.

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cent alloy gives 1750°–1755° (low sensitiveness); the 5 per cent, 1752°; and the 15 per cent, 1755°. The mean is 1752°.

TABLE XVI.—THERMAL E. M. F. AT MELTING-POINT OF PLATINUM.

| Date. | No. of element. | Rh in alloy wire. | Silver. | Platinum. |
|---|---|---|---|---|
| Day and Sosman: | | *p. ct.* | *mv.* | *mv.* |
| 1910, 19 February | F | 10 | 9103 | 18619 |
| 24 February | F | 10 | 9103 | 18613 |
| 25 February | Y | 10 | 9139 | 18695 |
| 25 February | Z | 10 | 9018 | 18487 |
| 8 March | J | 10 | 9106 | 18603 |
| 1 March | $I_1J$ | 1 | 1960 | 3560 |
| 15 April | KJ | 5 | 6495 | 12444 |
| 2 March | $I_{15}J$ | 15 | 10375 | 22303 |
| 4 March | $I_{15}J$ | 15 | 10375 | 22310 |
| Harker 1905 | N. P. L. 3 | 10 | (9084) | 18580 |
| Harker 1905 | T. 15 | 10 | (9100) | 18693 |
| Waidner and Burgess, 1907 | $P_2$ | 10 | (9024) | 18369 |
| Waidner and Burgess, 1907 | $P_3$ | 10 | (9040) | 18556 |
| Waidner and Burgess, 1907 | $S_1$ | 10 | (8991) | 18250 |

We did not personally undertake any measurements with radiation pyrometers, nor has any one yet had an opportunity to make use of our gas-thermometer temperatures for this purpose, but optical determinations of the *temperature interval* between palladium and platinum may be taken from the older observations without serious error so long as the absolute temperature values are not required. Thus, for example, we find:

TEMPERATURE INTERVAL PALLADIUM TO PLATINUM.

| | |
|---|---|
| Nernst and von Wartenberg (Berlin) | 204° |
| Holborn and Valentiner (at the Reichsanstalt) | 207° |
| Waidner and Burgess (at the Bureau of Standards) | 207° |
| Mean | 206° |

The mean value of this temperature interval from three good determinations is therefore 206°. Having fixed the palladium point on the nitrogen thermometer at 1549°, if we simply add 206° to this number we obtain a second extrapolated value of the platinum point at 1755°, in excellent agreement with the first.

The comparatively short interval over which extrapolation is now required (1550°–1750°) and the fact that two wholly independent methods yield temperatures for melting platinum which differ but 3°, gives to this extrapolation an appearance of trustworthiness which the earlier estimates have not possessed. The melting temperature of pure platinum may therefore be considered fairly secure at 1752° with an absolute error of perhaps ±5°.

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## 19. THE THERMO-ELEMENT CURVE FROM 0° TO 1755°.

Below 300° the sensitiveness of the platinum-platinrhodium element is very low compared with the platinum resistance thermometer, the copper-constantan thermo-element, or the mercury thermometer. Nevertheless, it is often convenient to use an available element for measurements in the lower range; hence we have in addition determined the course of the thermo-element curve from 0° to 300°.

The melting and boiling points of pure substances determined on the gas thermometer form the basis of this calibration as before. The 0° and 100° points are familiar. In the neighborhood of 200° and 300° the boiling-points of pure naphthalene and benzophenon were used. The only gas-thermometer determinations of these two points since the early and somewhat less accurate measurements by Crafts,[1] namely, those of Jaquerod and Wassmer,[2] differ from the values interpolated by Callendar and Griffiths[3] with the resistance thermometer, by 0.26° at 218° and 0.4° at 305°. The values of Jaquerod and Wassmer, which we have used, are 217.68° for naphthalene and 305.44° for benzophenon, at 760 mm. pressure.[4]

In our work with the gas thermometer, one measurement was made at the melting-point of cadmium, to give an indication of the course of the thermo-element curve in this lower region. Being only a single measurement, this has not as much weight as the higher temperatures, which were measured under varied conditions. The value obtained was 320.0°.

The difference between benzophenon and cadmium, determined with three platinum-platinrhodium thermo-elements, was found to be 14.8°. The benzophenon used was Merck's preparation, which boils 0.2° higher than the purest made by Kahlbaum. The difference between Kahlbaum's benzophenon and cadmium is then 15.0°, which is exactly the difference found by Waidner and Burgess at the Bureau of Standards, using a resistance thermometer.[5] On the basis of the benzophenon value adopted above, this difference makes the cadmium point 320.4°. We have arbitrarily connected the two portions of the temperature scale at this point by taking the mean, 320.2°, for cadmium. Since in this region temperatures can not be coveniently obtained closer than 0.2° with the platinum-platinrhodium element, the values are abundantly accurate for the present purpose.

It should not be overlooked that the value which we have obtained for zinc indicates a lower value for the boiling-point of sulphur than the figure 444.5° now in general use. The four independent gas-thermometer determinations that have been made of the sulphur point, although agreeing unusually well, are not free from the possibility of errors of several tenths of a degree, and this fact, taken together with the variability in the point itself with different experimental conditions, makes it probable that the absolute value given for the sulphur point is still somewhat uncertain.

[1] Bull. Soc. Chim., **39**, 277–289, 1883.
[2] Jour. Chim. Phys., **2**, 52–78, 1904.
[3] Phil. Trans. Roy. Soc., **182**, A, 43–72, 119–157, 1891.
[4] The results of Jaquerod and Wassmer have also been used as the standard since 1904 by the Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology, in their work on electrical conductivity at high temperatures.
[5] Bull. Bur. Stds., **7**, 1–9, 1910.

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## THERMO-ELEMENTS IN EVERY-DAY PRACTICE.

The summarized temperature scale adopted for present use in this laboratory for the calibration of thermo-elements is therefore as follows:

| | | | |
|---|---|---|---|
| Ice, m. p. | 0° | Gold, m. p. | 1062.4° |
| Water, b. p. | 100.0+0.037 (p−760) | Copper, m. p. (in CO) | 1082.6 |
| Napthalene, b. p. | 217.7+0.057 (p−760) | $Li_2SiO_3$ | 1201. |
| Benzophenon, b. p. | 305.4+0.063 (p−760) | Diopside, m. p. | 1391.2 |
| Cadmium, m. p. | 320.2 | Nickel, m. p. (in $N_2$) | 1452.3 |
| Zinc, m. p. | 418.2 | Cobalt, m. p. (in $N_2$) | 1489.8 |
| Antimony, m. p(inCO) | 629.2 | Palladium, m. p. | 1549.2 |
| Silver, m. p. (in CO) | 960.0 | Platinum, m. p. | 1755. |

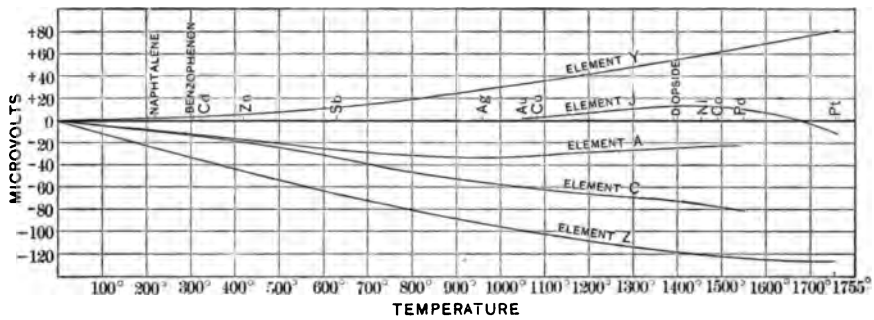


FIG. 15. Deviation of typical thermo-elements from standard curve.

For interpolation in every-day practice over this long range of temperatures we may use either an empirical equation or series of equations, or we may plot the temperatures and microvolts and draw a smooth curve through the points. The results of one method have no better claim to accuracy than the results of the other, for an empirical equation is essentially nothing but an imaginary curved ruler. A plotted curve on a scale large enough to get the requisite accuracy of reading would, however, take a sheet at least 30 feet square. But if instead of plotting microvolts directly against degrees, we plot the *deviation* from the straight line, $e = 10t$, the sheet required is reduced to about 3 feet square. If further, we plot the deviations of each element from an *arbitrary standard curve*, instead of the deviations from a straight line, the usual 50 cm. × 40 cm. sheet is ample.

The figures of Table XVII represent such a curve, which lies very close to the actual curve for the standard thermo-element E used in the work on the nitrogen thermometer. The deviations of various other elements, in use in the laboratory, from this standard are plotted in Fig. 15. These curves are obtained by plotting the differences between the reading of the element and that of the assumed standard at each calibration point.

An example will serve to make clear the method of converting microvolts into degrees with this table and curve. It is desired to find the temperature corresponding to a reading of 8931 microvolts on element Z. It is evident from the table that the temperature is in the neighborhood of 950°. At about this temperature, element Z reads 92 microvolts below the assumed standard; adding 92 microvolts to 8931 gives 9023 microvolts as the corresponding standard reading, and this by interpolation in the table gives 952.3°. The tenths, of course, mean little in absolute value; but temperature *differences*, in case measurements are made with similar elements under similar conditions, can be obtained if need be to tenths of a degree.

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TABLE XVII.—STANDARD CURVE OF ELEMENT Pt: (90 Pt 10 Rh) FROM 0° TO 1755°.

| *t* | *e* | Diff. | *t* | *e* | Diff. | *t* | *e* | Diff. |
|---|---|---|---|---|---|---|---|---|
| 0 | | 55 | 300 | 2315 | 92 | 580 | 5026 | 101 |
| 10 | 55 | 57 | *305.4 Benzo.* | *2365* | 93 | 590 | 5127 | 102 |
| 20 | 112 | 60 | 310 | 2407 | 93 | 600 | 5229 | 102 |
| 30 | 172 | 62 | 320 | 2500 | 93 | 610 | 5331 | 103 |
| 40 | 234 | 63 | *320.2 Cd* | *2502* | 93 | 620 | 5434 | 103 |
| 50 | 297 | 65 | 330 | 2593 | 94 | *629.2 Sb* | *5529* | |
| 60 | 362 | 67 | 340 | 2687 | 94 | 630 | 5537 | 103 |
| 70 | 429 | 69 | 350 | 2781 | 94 | 640 | 5640 | 104 |
| 80 | 498 | 71 | 360 | 2875 | 94 | 650 | 5744 | 104 |
| 90 | 569 | 72 | 370 | 2969 | 95 | 660 | 5848 | 104 |
| 100 | 641 | 73 | 380 | 3064 | 95 | 670 | 5952 | 104 |
| 110 | 714 | 75 | 390 | 3159 | 95 | 680 | 6056 | 105 |
| 120 | 789 | 77 | 400 | 3254 | 96 | 690 | 6161 | 105 |
| 130 | 866 | 78 | 410 | 3350 | 96 | 700 | 6266 | 105 |
| 140 | 944 | 79 | *418.2 Zn* | *3429* | 96 | 710 | 6371 | 106 |
| 150 | 1023 | 80 | 420 | 3446 | 96 | 720 | 6477 | 106 |
| 160 | 1103 | 81 | 430 | 3542 | 97 | 730 | 6583 | 106 |
| 170 | 1184 | 82 | 440 | 3639 | 97 | 740 | 6689 | 106 |
| 180 | 1266 | 83 | 450 | 3736 | 97 | 750 | 6795 | 107 |
| 190 | 1349 | 84 | 460 | 3833 | 98 | 760 | 6902 | 107 |
| 200 | 1433 | 85 | 470 | 3931 | 98 | 770 | 7009 | 108 |
| 210 | 1518 | | 480 | 4029 | 98 | 780 | 7117 | 108 |
| *217.7 Napht.* | *1584* | 86 | 490 | 4127 | 99 | 790 | 7225 | 108 |
| 220 | 1604 | 86 | 500 | 4226 | 99 | 800 | 7333 | 108 |
| 230 | 1690 | 87 | 510 | 4325 | 99 | 810 | 7441 | 109 |
| 240 | 1777 | 88 | 520 | 4424 | 100 | 820 | 7550 | 109 |
| 250 | 1865 | 89 | 530 | 4524 | 100 | 839 | 7659 | 110 |
| 260 | 1954 | 89 | 540 | 4624 | 100 | 840 | 7769 | 110 |
| 270 | 2043 | 90 | 550 | 4724 | 100 | 850 | 7879 | 110 |
| 280 | 2133 | 91 | 560 | 4824 | 101 | 860 | 7989 | 111 |
| 290 | 2224 | 91 | 570 | 4925 | 101 | 870 | 8100 | 111 |

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TABLE XVII.—STANDARD CURVE OF ELEMENT PT: (90 PT 10 RH) FROM 0° TO 1755°—Concluded.

| *t* | *e* | Diff. | *t* | *e* | Diff. | *t* | *e* | Diff. |
|---|---|---|---|---|---|---|---|---|
| 880 | 8211 | | 1170 | 11572 | | 1470 | 15183 | |
| | | 111 | | | 120 | | | 121 |
| 890 | 8322 | | 1180 | 11692 | | 1480 | 15304 | |
| | | 112 | | | 120 | | | 121 |
| 900 | 8434 | | 1190 | 11812 | | *1489.8 Co* | *15423* | |
| | | 112 | | | 120 | | | |
| 910 | 8546 | | 1200 | 11932 | | 1490 | 15425 | |
| | | 112 | | | 120 | | | 121 |
| 920 | 8658 | | 1210 | 12052 | | 1500 | 15546 | |
| | | 113 | | | 120 | | | 120 |
| 930 | 8771 | | 1220 | 12172 | | 1510 | 15666 | |
| | | 113 | | | 120 | | | 121 |
| 940 | 8884 | | 1230 | 12292 | | 1520 | 15787 | |
| | | 113 | | | 120 | | | 121 |
| 950 | 8997 | | 1240 | 12412 | | 1530 | 15908 | |
| | | 114 | | | 120 | | | 121 |
| 960 | 9111 | | 1250 | 12532 | | 1540 | 16029 | |
| | | 114 | | | 120 | | | 121 |
| *960.0 Ag* | *9111* | | 1260 | 12652 | | *1549.2 Pd* | *16140* | |
| | | | | | 120 | | | |
| 970 | 9225 | | 1270 | 12772 | | 1550 | 16150 | |
| | | 114 | | | 120 | | | 120 |
| 980 | 9339 | | 1280 | 12892 | | 1560 | 16270 | |
| | | 115 | | | 120 | | | 121 |
| 990 | 9454 | | 1290 | 13012 | | 1570 | 16391 | |
| | | 115 | | | 120 | | | 121 |
| 1000 | 9569 | | 1300 | 13132 | | 1580 | 16512 | |
| | | 116 | | | 120 | | | 120 |
| 1010 | 9685 | | 1310 | 13252 | | 1590 | 16632 | |
| | | 116 | | | 120 | | | 121 |
| 1020 | 9801 | | 1320 | 13372 | | 1600 | 16753 | |
| | | 116 | | | 120 | | | 120 |
| 1030 | 9917 | | 1330 | 13492 | | 1610 | 16873 | |
| | | 117 | | | 120 | | | 120 |
| 1040 | 10034 | | 1340 | 13612 | | 1620 | 16993 | |
| | | 117 | | | 121 | | | 120 |
| 1050 | 10151 | | 1350 | 13733 | | 1630 | 17113 | |
| | | 117 | | | 121 | | | 120 |
| 1060 | 10268 | | 1360 | 13854 | | 1640 | 17233 | |
| | | 118 | | | 121 | | | 120 |
| *1062.4 Au* | *10296* | | 1370 | 13975 | | 1650 | 17353 | |
| | | | | | 120 | | | 120 |
| 1070 | 10386 | | 1380 | 14095 | | 1660 | 17473 | |
| | | 118 | | | 121 | | | 120 |
| 1080 | 10504 | | 1390 | 14216 | | 1670 | 17593 | |
| | | 118 | | | 121 | | | 120 |
| *1082.6 Cu* | *10535* | | *1391.2 Diops.* | *14231* | | 1680 | 17713 | |
| | | | | | | | | 120 |
| 1090 | 10622 | | 1400 | 14337 | | 1690 | 17833 | |
| | | 118 | | | 121 | | | 120 |
| 1100 | 10740 | | 1410 | 14458 | | 1700 | 17953 | |
| | | 118 | | | 121 | | | 120 |
| 1110 | 10858 | | 1420 | 14579 | | 1710 | 18073 | |
| | | 119 | | | 120 | | | 120 |
| 1120 | 10977 | | 1430 | 14699 | | 1720 | 18193 | |
| | | 119 | | | 121 | | | 120 |
| 1130 | 11096 | | 1440 | 14820 | | 1730 | 18313 | |
| | | 119 | | | 121 | | | 120 |
| 1140 | 11215 | | 1450 | 14941 | | 1740 | 18433 | |
| | | 119 | | | 121 | | | 120 |
| 1150 | 11334 | | *1452.3 Ni* | *14969* | | 1750 | 18553 | |
| | | 119 | | | | | | 120 |
| 1160 | 11453 | | 1460 | 15062 | | *1755. Pt* | *18613* | |
| | | 119 | | | 121 | | | |

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The use of Table XVII and the deviation-curve (Fig. 15) avoids the calculation and recalculation of thermo-element curves and the tabulation of their readings. If the calibration of an element changes by a few microvolts, the deviation-curve is merely raised or lowered by a corresponding amount. If the value adopted for one of the calibration points is changed, the corresponding reading in microvolts of the assumed standard is also changed, and all the deviation-curves take a slightly different course in the neighborhood of that point. The table and curves make it possible, furthermore, to estimate temperatures (with an accuracy of perhaps 5°) with a new thermo-element, by simply calibrating it at, say, two points such as silver and diopside, and thus locating it among the family of deviation-curves.

## 20. RELATION OF THERMAL E. M. F. TO COMPOSITION.

In the course of the work on the nitrogen thermometer, the standard 10 per cent elements were compared with elements whose alloy wires contained 1 per cent and 15 per cent rhodium. The E. M. F. of the 20 per cent alloy, of which the bulb was made, was determined by two methods,[1] in order to evaluate the different readings on the nitrogen-thermometer bulb. To make the series more complete, a 5 per cent alloy was obtained from Heraeus and its readings against pure platinum were compared with the standards.

A similar series of comparisons was made in 1892 by Holborn and Wien,[2] using alloys with 9, 10, 11, 15, 20, 30, 40, and 100 per cent rhodium. This work was done, however, just at the beginning of the careful work of Mylius on the separation of the platinum metals, and the alloys then available were not pure. In the lower percentage alloys, different elements of the same nominal composition gave E. M. F.'s differing by 10 per cent or more, and varying differently with temperature. In the higher percentages, the E. M. F. varies little with the composition, and the results have therefore some value in indicating the course of the curve of E. M. F. and composition. The data have been corrected to our temperature scale, and also for the difference in E. M. F. standards.

Holborn and Day[3] in 1899 obtained the E. M. F. of pure platinum against two samples of pure rhodium up to 1300°. The data have been corrected to correspond to our temperature scale.

Waidner and Burgess[4] measured the E. M. F. of the 10 per cent against the 20 per cent alloy, at various points up to 1755°, using two samples. The addition of this value to the E. M. F. of the 10 per cent alloy against pure platinum gives an independent check on our direct measurements with the 20 per cent alloy. As shown by Fig. 16, the agreement is very good.

The summarized data are given in Table XVIII. For the 10 per cent alloy three values are given: first, the lowest-reading of the twelve elements used with the nitrogen thermometer; second, the highest-reading; and third, the standard element E.

The frequent comparisons of the platinum and platinrhodium wires of the standard 10 per cent elements during the work on the nitrogen thermometer, show that the differences among them are due partly to the platinum wire

[1] Page 67.
[2] L. Holborn and W. Wien, Uber die Messung hoher Temperaturen, Ann. Phys., 47, 107–134, 1892.
[3] Thermo-electricity in certain metals, Amer. Jour. Sci. (4), 8, 303–308, 1899; Ann. d. Phys. 2, p. 522, 1900. Sitzb. Berl. Akad., 1899, 691–695.
[4] Bull. Bur. Stds., 3, p. 200, 1907.

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and partly to the alloy. Element Z, for instance, reads lower than E chiefly because the platinum wire of Z is more impure than that of E; the effect of this impurity is partly neutralized by an apparently larger amount of rhodium in the alloy wire. This appears from the data in the table below, which show comparisons between several typical 10 per cent elements. The purest platinum appears to be that of J. If the thermo-electric effect of rhodium is proportional to its percentage from 0 to 1 per cent, then about 0.05 per cent rhodium in platinum wire would be sufficient to produce the difference between Z and E. The data are in microvolts.

TABLE XVIII.—THERMAL E. M. F. OF PURE PLATINUM AGAINST PLATINUM-RHODIUM ALLOYS, IN MILLIVOLTS.

| $t$ | 1 p. ct. | 5 p. ct. | 10 p. ct. | | | 15 p. ct. | 20 p. ct. | 30 p. ct.[1] | 40 p. ct.[1] | 100 p. ct.[2] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Low. | High. | Standard. | | | | | |
| 100° | 0.21 | 0.55 | 0.63 | 0.64 | 0.64 | 0.65 | ..... | ..... | ..... | 0.65 |
| 200 | 0.42 | 1.18 | 1.41 | 1.43 | 1.43 | 1.50 | ..... | ..... | ..... | 1.51 |
| 300 | 0.63 | 1.85 | 2.28 | 2.32 | 2.32 | 2.41 | ..... | 2.34 | 2.45 | 2.57 |
| 400 | 0.84 | 2.53 | 3.21 | 3.26 | 3.25 | 3.45 | 3.50 | 3.50 | 3.64 | 3.76 |
| 500 | 1.05 | 3.22 | 4.17 | 4.23 | 4.23 | 4.55 | 4.60 | 4.74 | 4.93 | 5.08 |
| 600 | 1.25 | 3.92 | 5.16 | 5.24 | 5.23 | 5.71 | 5.83 | 6.06 | 6.31 | 6.55 |
| 700 | 1.45 | 4.62 | 6.19 | 6.28 | 6.27 | 6.94 | 7.18 | 7.49 | 7.80 | 8.14 |
| 800 | 1.65 | 5.33 | 7.25 | 7.35 | 7.33 | 8.23 | 8.60 | 9.01 | 9.37 | 9.87 |
| 900 | 1.85 | 6.05 | 8.35 | 8.46 | 8.43 | 9.57 | 10.09 | 10.67 | 11.09 | 11.74 |
| 1000 | 2.05 | 6.79 | 9.47 | 9.60 | 9.57 | 10.96 | 11.65 | 12.42 | 12.94 | 13.74 |
| 1100 | 2.25 | 7.53 | 10.64 | 10.77 | 10.74 | 12.40 | 13.29 | 14.33 | 14.99 | 15.87 |
| 1200 | 2.45 | 8.29 | 11.82 | 11.97 | 11.93 | 13.87 | 14.96 | 16.39 | 17.13 | 18.10 |
| 1300 | 2.65 | 9.06 | 13.02 | 13.18 | 13.13 | 15.38 | 16.65 | 18.51 | 19.51 | 20.46 |
| 1400 | 2.86 | 9.82 | 14.22 | 14.39 | 14.34 | 16.98 | 18.39 | 20.67 | 21.73 | ..... |
| 1500 | 3.06 | 10.56 | 15.43 | 15.61 | 15.55 | 18.41 | 20.15 | ..... | ..... | ..... |
| 1600 | 3.26 | 11.31 | 16.63 | 16.82 | 16.75 | 19.94 | 21.90 | ..... | ..... | ..... |
| 1700 | 3.46 | 12.05 | 17.83 | 18.03 | 17.95 | 21.47 | 23.65 | ..... | ..... | ..... |
| 1755 | 3.56 | 12.44 | 18.49 | 18.70 | 18.61 | 22.31 | 24.55 | ..... | ..... | ..... |

[1]Holborn and Wien, 1892, loc. cit. [2]Holborn and Day, mean value, 1899, loc. cit.

The data of Table XVIII are plotted in Fig. 16, which shows the relation between temperature and thermal E. M. F. for various alloys. The 30 per cent and 40 per cent curves represent the data of Holborn and Wien. The curve for pure rhodium represents the mean of the two samples by Holborn and Day. There is no indication of a break in any of the curves over the entire range of temperature.

In Fig. 17, the data of Table XVIII are plotted to show the relation of the thermal E. M. F. at various constant temperatures to the composition of the alloy wire, the cold junction being in every case at 0°. At all tem-

| Element. | E. M. F. of Pt wire against Pt of E at 1500°. | E. M. F. of Pt-Rh wire against Pt-Rh of E at 1500°. | Difference between elements. |
|---|---|---|---|
| Y | + 12 | +75 | + 63 |
| Z | +177 | +67 | −110 |
| A | + 75 | +47 | − 28 |
| F | + 7 | + 1 | − 6 |
| J | − 9 | + 1 | + 10 |

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peratures the E. M. F. increases very rapidly with the first additions of rhodium, and at 20 per cent the value has already reached 81 to 93 per cent of the E. M. F. of platinum against pure rhodium.

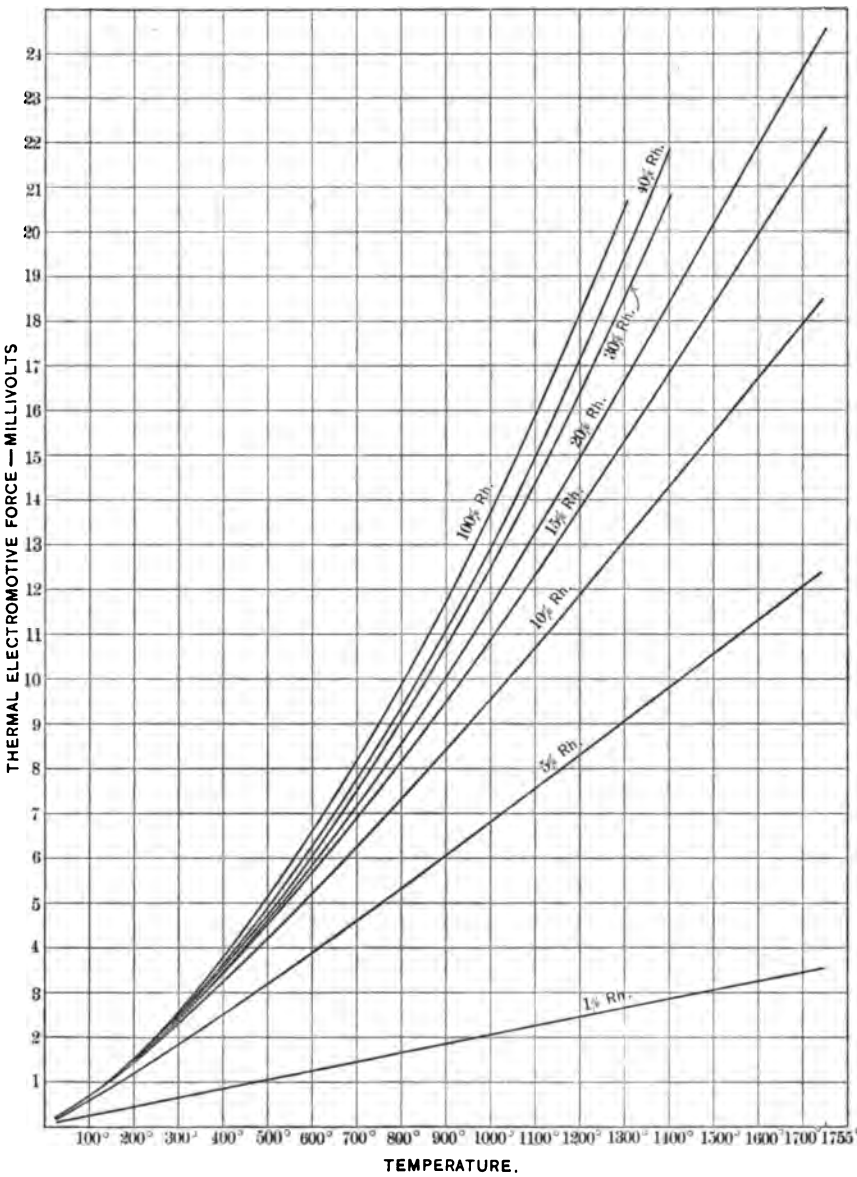


FIG. 16. Relation of temperature to thermal electro-motive force of platinum against platinum-rhodium alloys.

The thermo-electric power, or rate of change of E. M. F. with temperature $\frac{de}{dt}$ is plotted in Fig. 18, against the atomic concentration of the alloy. The values are in microvolts, against pure platinum. The curves for all tem-

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peratures are similar in form and approach the curve for 1755° as an envelope.

In a recent study of the thermo-electric properties at low temperatures of the alloys of tellurium with antimony, tin, and bismuth, and of antimony with silver, Haken[1] comes to the conclusion that a thermo-electric curve of the form of those in Fig. 18 accompanies the formation of a solid solution between the end components, while compounds are marked by sharp maxima or minima. The thermo-electric curves of the systems copper-cobalt, by Reichardt;[2] copper-nickel, by Feussner and Lindeck;[3] and silver-zinc, by Puschin and Maximenko,[4] show a similar relationship between the form of the curve and the constitution of the alloy. More recently, E. Rudolfi[5] has published a study of these relationships for eight pairs of metals.

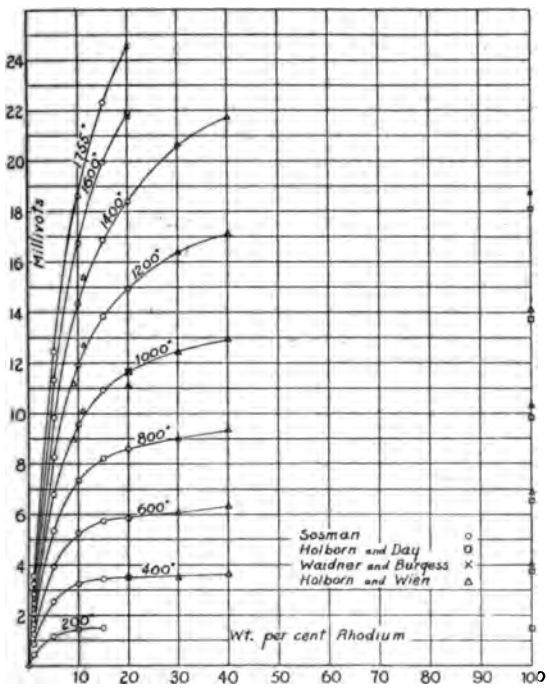


FIG. 17. Relation of thermal electromotive force, $\epsilon$, to composition of platinum-rhodium alloys.

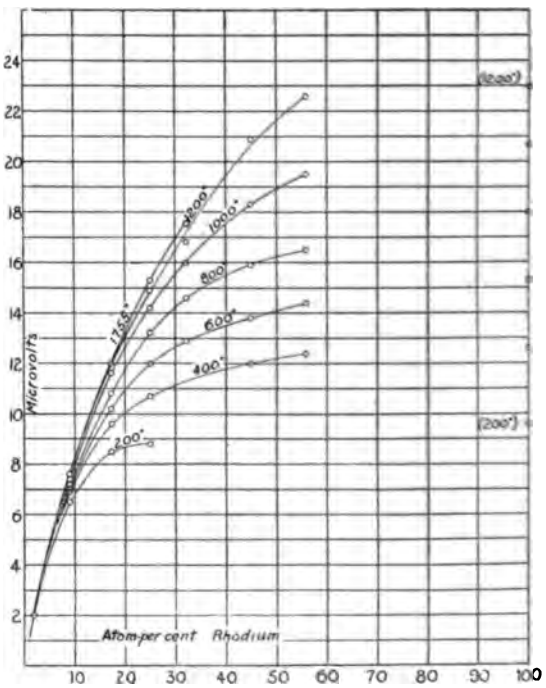


FIG. 18. Relation of $\frac{d\epsilon}{dt}$, thermo-electric power against platinum, to atomic composition.

The alloys of platinum and rhodium have not been studied microscopically or thermally, but measurements in our carbon-tube furnace showed that the melting-points of the 1 per cent and 5 per cent alloys are higher than 1755°. The melting-point of the 10 per cent alloy is given by von Wartenberg[6] as 1830°, and of pure rhodium as 1940°. It is very probable, therefore, that platinum and rhodium form solid solutions at least as far as 55 atomic per cent rhodium, with no compounds, over the range of temperature covered by our data.

[1] Verh. deutsch. phys. Ges. **12**, 229–239, 1910. Ann. d. phys., **32**, 291–336, 1910.
[2] Ann. d. Phys., **6**, 832–55, 1901.
[3] Wiss. Abh. Phys.-Tech. Reichsanstalt, **2**, p. 515. 1895.
[4] Jour Russ. Phys. Chem. Ges., **41**, 500–524, 1909.
[5] Zeitschr. anorg. Chem., **67**, 65–96, 1910.
[6] Verh. Deutsch. Phys. Ges., **12**, 121–127, 1910.

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## 21. SUMMARY.

It is now something over five years since the Geophysical Laboratory took up the task of redetermining the absolute temperature scale from 400° to 1100° with the nitrogen thermometer, and of extending it, if it should prove practicable to do so, to 1600° C., covering the region in which are found most of the mineral relations which it is the chief purpose of the laboratory to study. Two preliminary publications have been made during the investigation. One, a brief summary of preliminary work up to 1100°, was given before the National Academy of Sciences and the American Physical Society in April, 1907;[1] the second covered the same ground at considerable length in 1908.[2] A final paper[3] extending the observations to 1550°, and a supplementary paper[4] on the use of thermo-elements throughout the entire range from zero to melting platinum appeared in 1910 and completed the work contemplated under the original plan.

The gas-thermometer problem at the present stage of its development has become primarily a problem for experimental study with two definite purposes, one to increase the accuracy of the measurements, the other to increase their range. The application of the gas laws is no longer subject to serious question. The progress of recent years has given us electric heating in place of gas and the consequent possibility of controlling the temperature with great certainty and exactness. It has also given us the metal bulb with a definite and measurable expansion coefficient and capable of holding the expanding gas without loss. It has discovered a gas which does not diffuse through the bulb or react with it chemically, which does not dissociate within the limits of practicable measurement, and of which the expansion can be expressed with reasonable certainty in terms of the Kelvin thermodynamic scale whenever it may prove necessary or desirable to do so. It has also discovered the source of the errors in the thermo-elements and a way to avoid them.

In 1904 Professor Holborn of the Reichsanstalt increased the range of this scale as far as 1600° C., the probable error of the new portion being 10°. Simultaneously with this effort, work was begun at the Geophysical Laboratory in Washington with a view to increasing the accuracy of the scale, first over the existing range (to 1150°), and later, as much beyond this point as it should prove practicable to go.

No attempt will be made to offer an inclusive summary of the whole investigation. It is a record of experimental measurements covering an unusually wide range of details which do not admit of brief classification. The errors which have heretofore been present in measurements with the nitrogen thermometer have been reduced by the present investigation to about one-fourth their former magnitude and the certainty of their evaluation is at least proportionately increased.

The particular points to which we have given most attention are the following:

(1) To provide a uniform temperature about the bulb by a suitable arrangement of electric-heating coils and diaframs.

[1] Abstract, Phys. Rev., **24**, 531, 1907.
[2] Amer. Jour. Sci. (4), **26**, 405–463, 1908.
[3] Amer. Jour. Sci. (4), **29**, 93–161, 1910.
[4] Amer. Jour. Sci. (4), **30**, 1–15, 1910.

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(2) To inclose the furnace in a gas-tight bomb in which the pressure outside the bulb can be maintained equal to that within for all temperatures. This offers three distinct advantages: (*a*) it provides against the deformation of the bulb through differences of pressure within and without in the region of highest temperatures, where the bulb material becomes softer; (*b*) by using the same gas within and without, there is no tendency for it to diffuse through the bulb wall; (*c*) it enables the initial pressure to be varied within considerable limits, thereby increasing both the scope and sensitiveness of the manometer. The sensitiveness in our instrument with this arrangement was about three times that of the Reichsanstalt.

(3) The expansion of the bulb material was determined with great care and is probably accurate within 0.5 per cent.

(4) The unheated space between the bulb and manometer has been reduced until the total correction in this hitherto uncertain region amounts to less than 4° at 1100°. An error of 5 per cent in the determination of its volume or temperature distribution is, therefore, practically negligible.

It is probable that these changes serve to reduce the uncertainty hitherto prevailing in the correction factors which require to be applied to the gas thermometer in the region of 1100° to less than one-tenth of its former magnitude. Furthermore, these improvements are equally applicable throughout the region above 1100° as far as the present measurements have extended (to 1550°).

The chief source of present uncertainty is the temperature distribution over the surface of the bulb in an air bath. It would be possible to eliminate this error in the lower portion of the scale by substituting a liquid bath which could be stirred. In fact, this was done for temperatures below 500° in the earlier work of Holborn and Day, but has not so far been tried in the present investigation because of the relatively secondary importance of the lower temperatures to the ultimate purpose of the investigation (the study of silicates). For the higher temperatures no satisfactory liquid bath has been found.

The treatment of experimental errors in a complicated problem of this kind is obviously a matter into which the personal equation enters largely. The only sure method is to make their total magnitude disappearingly small, and to this end our efforts have been directed wherever possible. Errors due to failure of the pressure to return to its initial zero after heating to a high temperature, which are due to permanent changes in the volume of the bulb, or to absorption or loss of gas, are entirely negligible in the present instrument. This source of error is of a particularly intangible kind and has clung to all the earlier work in gas thermometry like a haunting evil spirit.

Another classical source of uncertainty to which attention has already been called, lies in the unheated connecting link between the hot bulb and cold manometer in which the volume and temperature conditions have been exceedingly difficult to establish. It is also reduced to practically insignificant magnitude in the present instrument and can be still further diminished if necessary.

Still a third difficulty which was discovered in this laboratory[1] soon after

[1] W. P. White, "The Constancy of Thermo-elements," Phys. Rev., **23**, 449–474, 1906.

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this investigation began and which at once assumed serious proportions, arises from the gradual contamination of the auxiliary thermo-elements by iridium vapor from the heating coil, the bulb, or any platinum crucibles or diaframs containing this metal which are exposed by accident or design in the furnace at extreme temperatures. This absorption of iridium vapor (in a minor degree of rhodium vapor also) which has been an important though unrecognized factor in all previous work in which thermo-elements were used (beginning with Barus), has the effect of making the thermo-elements read lower as contamination increases. These effects also have been reduced to negligible magnitude in all the observations of the present series subsequent to the preliminary set (Table II), which has not been used in calculating the results.

The remaining correction factors are numerous, but with the exception of the expansion of the bulb, which has been very carefully determined, are not only small but are unlikely to become cumulative in a particular case. The temperature correction for the mercury columns of the manometer, for example, which is of a magnitude to catch the eye in the table on p. 69, and to which our attention has been explicitly called, is in fact an error of very harmless character in practice in the magnitude in which it here enters. It appears as an error of the same order of magnitude and same sign in two quantities, the difference of which is used in the computation of temperature. It varies but little in the observations of a single day and does not increase with the temperature. There is therefore little of real uncertainty to be apprehended from this source. The same is true of many of the other minor corrections to which the final values are subject.

In general it may be said, for the information of those who have not a first-hand acquaintance with the gas thermometer, that the danger lies in relations which become more uncertain as the temperature advances, such for example as the distribution of temperature about the bulb, which is continually changing in an air bath at extreme temperatures, and in the expansion of the bulb material in the same region. Changes in the temperature of the bulb wall can be observed by grouping a number of thermo-elements about it (eight were used for this purpose in our experiments) and corrections can be applied for the differences observed. In the experiments here recorded the temperature control was very perfect, even at the highest temperatures, and differences of temperature on the surface of the bulb amounting to a whole degree were rarely observed.

It is, however, a little difficult to make positive assertions about the temperature of the gas in a containing vessel when the temperature on its surface shows differences of 10 degrees or more, as has usually been the case in the earlier high-temperature gas-thermometer measurements. The same may be said of the expansion of the bulb itself; a determination of the expansion coefficient, however accurate for the range of temperatures from zero to 100°, or to 500°, affords insufficient basis for an extrapolation to 1600°, particularly since the expansion has been definitely shown not to be a linear function, but to increase with some rapidity with the temperature in the case of the platinum alloys which serve the purpose best. Such haphazard extrapolation appears particularly rash when it is recalled that this is

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the most important and largest correction factor to which gas-thermometer observations are now subject and one which can not be avoided or materially diminished in magnitude. Inasmuch as the bulb itself is practically inaccessible for the purpose of measuring its expansion, this difficulty was met in the present experiments by having a half-meter bar made up at the same time as the bulb and from the same material. The linear expansion of this bar was measured directly in a special form of comparator (p. 27) up to 1400°; beyond this temperature the bar sagged under its own weight and accurate measurements were no longer practicable. From 1400° to 1550°, therefore, we were also obliged to resort to extrapolation; but with consistent measurements (maximum difference 0.5 per cent), several times repeated at every 50° interval from 300° to 1400°, the extrapolation over an additional 150° appears reasonably free from uncertainty unless indeed the alloy should be found to possess an inversion point in that region. But such a point would certainly show itself in the form of a break in the series of gas-thermometer observations themselves and probably also in the electromotive force of thermo-elements of this composition, and of such irregularities the observations reveal no trace.

By way of conclusion of this effort to reduce uncertainty to a minimum, a final attempt was made by the present observers to ascertain the order of magnitude of the aggregate uncertainty in the results at 1100° by experimental means. A new furnace was prepared with a very thick (1 inch) wall (the original furnaces had no wall inside the heating coil) and wholly different arrangements for distributing the heat within it (see Fig. 10 and description, p. 56). In this furnace all the correction factors which result from heat distribution and the contamination of thermo-elements from the heating coil were radically altered, but the temperature measurements at the copper melting-point agreed with the mean of all the determinations at this temperature identically (1082.6°).

The interpretation of these measurements in terms of the melting-points of readily available substances encounters certain difficulties. The melting-point of pure salts is not sufficiently sharp and is somewhat difficult of interpretation. The metals which have commonly been used for the purpose, with the possible exception of nickel and cobalt, are, however, obtainable in sufficiently uniform purity to guarantee an accuracy within 1° at the higher temperatures.

No effort has been made to prepare metals in our own laboratory of exceptional purity, for the reason that such metals would not be available for general use and would therefore be of little service. We have accordingly adopted metals which are carried permanently in stock by dealers whose names are given in connection with each, from whom the same metal in a nominal quality equal to that which we used can be readily obtained. We have analyzed these with extreme care to show the exact content of the sample supplied us. We have duplicated the purchases ourselves, and have found no errors greater than 1° in their melting-point determinations.

Another difficulty arises from the fact that the melting-points of the purest metals available for use as constants in reproducing a high-temperature scale (zinc, silver, gold, copper, and palladium) are distributed in such a way that, although they may be *located* upon the gas-thermometer

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scale with a probable error not greater than 0.5° at low temperatures or 1° at high temperatures, the calculation of a similar curve passing through these points may not suffice to *reproduce* the scale with this accuracy. In the region midway between zinc (418.2°) and silver (960.0°) the error of interpolation may amount to 2°, and between copper and palladium to 5°, even with metals of exceptional purity. Extrapolation is even more uncertain. This can be avoided by locating a sufficient number of intermediate points which are equally trustworthy, if such can be found. We have not been fortunate enough to find points which fulfil these conditions quite as well as the metals named above, but if the table (Table XVII) offered in the text is accurately followed, there is little danger of serious errors, even in inexperienced hands.

In order to facilitate as far as possible the application of these results in general practice, a typical thermo-element curve has been tabulated in small 10° intervals throughout its entire length from melting ice to melting platinum, together with a diagram showing the character and magnitude of the variation from this curve, which may be expected to appear in other thermo-elements of the same nominal composition (90 parts platinum, 10 parts rhodium). With a new platin-rhodium thermo-element of undoubted homogeneity, but unknown constants, it is quite practicable with this table to prepare a curve of its electromotive force for any temperature with sufficient accuracy for most purposes (say 5° at low temperatures and ± 10° above 1200°) from a single determination in melting copper. If this accuracy is inadequate, additional determinations of its electromotive force at other temperatures of the list below will help to fix it more closely.

There is no sure way to guard against the contaminating influence of metal vapors upon a thermo-element in laboratory or industrial practice, although glazed porcelain is usually effective. There are very simple and rapid means of detecting contamination in an element and determining its distribution, and with a second element at hand for an occasional comparison there is little of serious danger from this cause. In any case, the slight inconvenience is well worth while wherever considerable accuracy is sought, for there is no other device yet available, in the region between 1100° and 1600°, which is comparable with the thermo-element in sensitiveness and general practicability.

In conclusion, the list of standard melting-points is given in tabular form, together with an estimate of the degree of trustworthiness to be accorded to each. Beside it for convenient comparison is the present Reichsanstalt scale. It may be added that no indication of a limit to the temperature attainable with the nitrogen thermometer or to its ultimate accuracy was discovered during the present investigation.

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TABLE XIX.

| Substance. | Point. | Atmosphere. | Crucible. | Temperature. | Reichsanstalt scale. |
|---|---|---|---|---|---|
| Zinc | Melting and freezing | Air | Graphite | 418.2° ±0.3 | 419.0° |
| Antimony | Do | Carbon monoxide | Do | 629.2 ±0.5 | 630.6 |
| Silver | Do | Do | Do | 960.0 ±0.7 | 961.5 |
| Gold | Do | Do | Do | 1062.4 ±0.8 | 1064.0 |
| Copper | Do | Do | Do | 1082.6 ±0.8 | 1084.1 |
| Diopside (pure) | Melting | Air | Platinum | 1391.2 ±1.5 | |
| Nickel | Melting and freezing. | Hydrogen and nitrogen. | Magnesia and magnesium aluminate. | 1452.3 ±2.0 | |
| Cobalt | Do | Do | Magnesia | 1489.8 ±2.0 | 1575.[1] |
| Palladium | Do | Air | Pure magnesia | 1549.2 ±2.0 | |
| Anorthite (pure) | Melting | Do | Platinum | 1549.5 ±2.0 | |

In addition, the following temperatures were incidentally obtained:

| | | | | | |
|---|---|---|---|---|---|
| Cadmium | Melting and freezing. | Air | Graphite | 320.0° ±0.3 | 321.7 |
| Aluminum | Freezing | Carbon monoxide | Do | 658.0 ±0.6 | 657. |
| $Li_2SiO_3$ | Melting | Air | Platinum | 1201. ±1. | |
| Platinum | Melting | Air | | 1752[2] / 1755[3] ±5. | |

[1] Holborn and Valentiner, loc. cit. [2] Extrapolation, thermo-electric. [3] Extrapolation, optical.

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